Ultraviolet-Printing-Assisted Surface-Confined Growth of Silver Nanoparticles on Flexible Polymer Films for Cu^{2+} and H_2S Sensing

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ABSTRACT: Metal nanoparticles (NPs) confined on the surface of flexible polymers films are highly sought after for a diverse range of applications. Herein, we report a facile substrate-independent strategy for surface-confined growth of silver NPs (AgNPs) on the surfaces of chemically diverse flexible polymer film substrates represented by polypropylene (PP), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). The surfaces of polymer films were subjected to ultraviolet-printing and conjugated to the hyperbranched polyethyleneimine (PEI). The PEI-functionalized surfaces were subjected to surface-confined growth of AgNPs via three approaches. Besides PEI, the ability of quaternary amine and carboxylic acid functional groups to assist surface-confined growth of AgNPs is also evaluated. All the films with surface-confined AgNPs exhibited absorbance due to the surface plasmon resonance (SPR) characteristic of AgNPs. The AgNPs confined on the surface of PP films were functionalized with 4-mercaptobenzoic acid, and the λ_{max} for SPR absorbance of the resulting platform was found to exhibit a markedly higher bathochromic shift when exposed to Cu^{2+} ions. This Cu^{2+} ions sensor could sense Cu^{2+} ions with a limit of detection of 2.6 ppm. Besides Cu^{2+} sensing via a bathochromic shift in λ_{max} for SPR absorbance, the SPR absorbance of AgNPs confined on the surface of PP films was found to diminish upon exposure to the aqueous solution of sodium hydrosulfide (NaSH), which acts as a hydrogen sulfide (H_2S) donor. The intensity of the SPR absorbance was found to decrease >40% upon exposure to 5 μM aqueous NaSH solution, whereas the SPR signal almost completely disappeared with visual decoloration when the films were exposed to 50 μM aqueous NaSH solution. This highlights the H_2S sensing ability of the AgNPs confined on the surface of PP films. In brief, this study is a step toward the future development of flexible chemical sensor platforms and beyond.

KEYWORDS: surface-confined nanoparticles, silver nanoparticles, flexible polymer films, chemosensor, flexible sensors

1. INTRODUCTION

Flexible polymer films with surface-confined or embedded silver nanoparticles (AgNPs) are the focus of extensive scientific interest, augmenting a wide range of technologies including flexible printed electronics,^{1–6} energy storage,⁷ energy-producing technologies,^{8–14} catalysis,^{15–17} biomedicine,^{18–20} flexible sensors,^{21,22} and smart surfaces (e.g., self-cleaning, antimicrobial, and anti-counterfeiting).^{23–26} Confining metal NPs on the surface of flexible polymer films integrates the unique electronic and optical properties of NPs stemming from their small size with low production cost, relatively lower density, inherent flexibility, and diverse functionalities associated with the polymer. In addition, surface-immobilized NPs do not suffer from the aggregation-induced decay of their functionality, which is quite common to the aqueous or organic NPs suspensions. Consequently, mastering the surface confinement of AgNPs remains an active area of research enabling a range of existing and future technologies. In this context, surface immobilization of

presynthesized AgNPs is a frequently explored strategy. In this vein, presynthesized AgNPs have been immobilized on the surfaces of a glass slide, silicon wafer, and flexible polymeric substrate via drop casting and spin coating without employing any surface pretreatment.^{27,28} In addition, plasma treatment has been employed to enhance the electrostatic interaction between flexible substrates and presynthesized nanomaterials.²⁹ The assemblies of NPs prepared by physical deposition techniques generally exhibit poor stability and can shed off easily from the surface of the substrate due to the lack of chemical bonding and physical tethering forces, and as a result, performance degradation is inevitable. Alternatively, substrates

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can be pretreated to display specific surface functionalities for noncovalent or covalent surface immobilization of presynthesized AgNPs. Pyridine,³⁰ thiol,³¹ amine,^{32,33} or carboxylic acid¹⁶ functional groups are known to act as ligands for metals and metal ions, and substrates can be pretreated to display these functional groups and assist in the surface immobilization of AgNPs. Covalent immobilization of AgNPs has been realized via common organic coupling reactions between appropriately surface-functionalized NPs and polymer substrates.^{34,35} In contrast to the strategies employing presynthesized NPs, AgNPs can also be conveniently grown from the surfaces of appropriately functionalized substrates. These so-called *in situ* strategies involve exposure of the substrates that are surface-functionalized with ion chelating functional groups to the solution of AgNPs precursor ions (Ag^+). This results in the adsorption of Ag^+ ions on the substrate surface, which are subsequently reduced to AgNPs either by exposing the substrate surface to an external reducing agent in a sequential manner or via the intrinsic reducing ability of the chelating functional groups. In the case of the sequential approach, sodium borohydride (NaBH_4) is commonly used as an external reducing agent.³⁶ Interestingly, amines, carboxylic acid groups, and ethylene glycol functionalities are known to simultaneously adsorb Ag^+ ions and reduce them to AgNPs.³⁷ These functionalities can be chemically introduced on the surfaces to achieve surface-confined growth of AgNPs. A variety of synthetic polymers exhibiting the ability of simultaneously chelating and reducing metal ions have been identified, and these include poly(vinylpyrrolidone) (PVP),^{38,39} poly(ethylene glycol) (PEG),^{40,41} poly(amidoamine) (PAMAM),⁴² poly(propyleneimine) (PPI),^{43,44} and poly(ethyleneimine) (PEI).^{45–47} Immobilizing these polymers on the surface of a substrate followed by exposure to Ag^+ ions can result in surface-confined growth of AgNPs. Besides synthetic systems, redox properties of nature-inspired polydopamine (PDA) coatings have been employed as simultaneous chelating and reducing functionalities.^{19,48–50} Comparing all the described approaches employing presynthesized NPs with the *in situ* approaches, the *in situ* approaches offer the advantages of bypassing the solution synthesis of NPs as well as potentially offer a higher surface density of the surface-confined NPs. However, both the approaches require surfaces with appropriate surface chemical nature. Therefore, it is evident that an appropriate surface chemical nature is necessary to either surface-immobilize presynthesized AgNPs or initiate a surface-confined growth of AgNPs. The flexible polymer film substrates come in a wide variety as far as their chemical nature is concerned. Despite the convenience offered by the *in situ* approach, the surface chemical nature of the flexible polymer film substrates is not always suitable to support surface-confined growth of AgNPs or any other metal NPs for that matter. Although the surface chemistry of polymer film substrates can be modulated by employing wet chemical reactions, diversity in the chemistry of polymer films means that a diverse range of wet chemical reactions would be required. Alternatively, a range of surface functionalization strategies can be applied to impart specific functionalities on the surface of chemically diverse polymer substrates in a substrate-independent manner. These strategies include combinations of ultraviolet/ozone (UVO) treatment, plasma polymerization, surface-initiated polymerization (SIP), photolithography, and UV-printing. Employing these strategies, a wide variety of chemically diverse polymer film substrates

including polyether ether ketone (PEEK), polyethylene terephthalate (PET), polyimide (PI), poly(tetrafluoroethylene) (PTFE), polycarbonate (PC), and polypropylene (PP) have been functionalized to achieve surfaces displaying antifouling, thermo/pH responsive wettability, electrostatic interactions, patterned cell growth, and surface-confined growth of catalytically active metal NPs.^{51–53} Capitalizing on these strategies, herein we report a substrate-independent approach to functionalize the surfaces of three chemically distinct polymer film substrates, namely, PP, PVC, and PET to make them suitable for initiating surface-confined growth of AgNPs. To achieve this goal, we have applied a combination of UVO-assisted surface oxidation, silanization, and UV-printing to functionalize the surfaces of PP, PVC, and PET with isocyanate groups, which were subsequently functionalized with PEI. The surface PEI moieties were employed to initiate surface-confined growth of AgNPs. The process of surface-confined AgNPs growth was thoroughly optimized for reaction time and influence of external reducing agents to reveal the evolution of surface density and size of surface-confined AgNPs. In addition, the ability of quaternary amine and carboxylic acid functional groups to support surface-confined growth of AgNPs was also investigated. The process of surface-confined AgNPs growth optimized on the surface of PP was extended to PVC and PET polymer film substrates. The sensitivity of the SPR displayed by the surface-confined AgNPs toward the changes in the chemical nature of the environment was used to develop PP-based flexible strips as sensors for copper ions (Cu^{2+}) and aqueous hydrogen sulfide (H_2S). Combining the versatility of UV-printing techniques and the convenience of the surface-confined growth of NPs, this work offers a new avenue to flexible polymer film substrate-based chemical sensor platforms.

2. MATERIALS AND METHODS

2.1. Materials. PP (20 μm), PVC (30 μm), and PET (30 μm) films were kindly supplied by local companies Tri-Pack Films Limited, ATS Synthetic Private Limited, and Carvan Plastics Private Limited, respectively. 2-Isocyanatoethyl methacrylate (ICEMA, 98%), branched polyethyleneimine (PEI, MW $\sim 25,000$ by LS), triethylamine (NEt_3), sodium borohydride (NaBH_4 , $\geq 96\%$), copper (II) chloride (CuCl_2 , 98%), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 98%), sodium hydrosulfide hydrate (NaSH), sodium iodide (NaI , $\geq 99.5\%$), and cobalt(II) acetate tetrahydrate ($(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$) were purchased from Sigma Aldrich, Germany. 3-(Trimethoxysilyl)propyl acrylate (TMSPA, $>93\%$), trimethylolpropane triacrylate (TMPTA, $>85\%$), Irgacure 184 (IRG 184), 4-mercaptobenzoic acid (MBA, $>95.0\%$), choline chloride (CC, $>98\%$), and potassium iodide (KI, $>99.5\%$) were supplied by TCI Japan. Silver nitrate (AgNO_3) was bought from Fisher Chemical. Nickel(II) nitrate hexahydrate (98%) and poly(acrylic acid) (PAA, 25% soln in H_2O) were purchased from Alfa Aesar, Germany. All the chemicals were used as received without any further purification.

2.2. Surface Modifications of Polymeric Films. **2.2.1. UV Printing.** Polymer films were cut into strips of $3 \times 3 \text{ cm}^2$ and subjected to ultraviolet ozone (UVO) treatment for 5 min. The films were immediately treated with a 2% solution of TMSPA in methanol at room temperature for 5 min. The samples were then dried under ambient conditions to remove any solvent residue. TMSPA-functionalized films are designated as PP-TMSPA, PVC-TMSPA, and PET-TMSPA. The TMSPA-functionalized films were subsequently coated via UV printing. The UV curable solution mixture consisted of a monomer (ICEMA, 80 wt %), cross-linker (TMPTA, 19 wt %), and photoinitiator (IRG 184, 1 wt %). Photopolymerization was performed for 4 min in a UV chamber BS-03. The UV-printed

Scheme 1. (A) Schematic Illustration of UV-Printing of Reactive Coatings on the Surface of Flexible Polymer Film Substrates Followed by Functionalization with PEI, CC, and PAA. (B) Assessment of Flexible Polymer Film Substrates with Surface-Confined AgNPs for (a) Cu^{2+} and (b) H_2S Sensing

films displaying $-\text{NCO}$ groups on their surfaces were designated as PP-NCO, PVC-NCO, and PET-NCO.

2.2.2. Functionalization of UV-Printed Films with PEI. UV-printed polymer films were functionalized with PEI under basic conditions. A solution containing PEI (30 wt %), triethylamine (TEA) (15 wt %), and deionized water (55 wt %) was applied to the surface of UV-printed polymer films and left to react for 4 h at 60 °C. The samples were then rinsed with excess water and dried under a vacuum. PEI-functionalized films were designated as PP-PEI, PVC-PEI, and PET-PEI.

2.2.3. Functionalization of UV-Printed Films with CC. UV-printed PP films were covered with a solution containing choline chloride referred to as CC (30 wt %), TEA (15 wt %), and deionized water

(55 wt %) and left for 4.5 h at 50 °C. CC molecules possess alcohol groups, which conjugate to the surface isocyanate groups via urethane linkage. Finally, the samples were washed with excess water and dried under a vacuum. CC-functionalized PP films were designated as PP-CC.

2.2.4. Functionalization of UV-Printed Films with PAA. UV-printed PP films were covered with a solution containing PAA (30 wt %), TEA (15 wt %), and deionized water (55 wt %) and left to react for 2.5 h at 50 °C. Finally, the samples were washed with excess water and dried under a vacuum. PAA-functionalized PP films were designated as PP-PAA.

2.3. Surface-Confined Growth of AgNPs. Surface-confined growth of AgNPs was achieved by employing three approaches. The

process was optimized on PP-PEI, and the optimized protocol was applied to other films. In the first approach, an aqueous solution of AgNO_3 (0.3 M) was placed on the surface of PP-PEI films and left for 3 h at room temperature. In the second approach, PP-PEI films were exposed to AgNO_3 (0.3 M) solution for 1 h, after that an aqueous solution of NaBH_4 (0.2 M) was also added to the AgNO_3 solution that was placed on top of the PP-PEI films. In the third approach after exposure to AgNO_3 (0.3 M) for 1 h, the AgNO_3 solution was blotted out, and PP-PEI films with Ag^+ ions adsorbed on their surfaces were exposed to an aqueous solution of NaBH_4 (0.2 M) by simply placing NaBH_4 solution on top of the films. The films were then rinsed with deionized water, dried, and stored under ambient conditions. The third approach was applied to grow AgNPs on the surfaces of PVC-PEI and PET-PEI films. For the proof of concept, the first and third approaches were also applied to grow AgNPs on the surface of PP-PAA and PP-CC. AgNPs-functionalized films were designated as PP-PEI-AgNPs, PVC-PEI-AgNPs, PET-PEI-AgNPs, PP-PAA-AgNPs, and PP-CC-AgNPs.

2.4. Functionalization of PP-PEI-AgNPs Films with 4-MBA. PP-PEI-AgNPs films were immersed in 1 mM methanol solution of 4-MBA and left to react for 2 h at 0 °C, allowing the self-assembly of 4-MBA on the surface of AgNPs. After that, the films were removed from the reaction mixture, washed with methanol, and dried under a vacuum. The resulting film was designated as PP-PEI-AgNPs/MBA.

2.5. Cu^{2+} Ion Sensing. A stock solution of CuCl_2 (1 mM) was used to prepare standard solutions of Cu^{2+} ions in a range of 1–100 ppm. The PP-PEI-AgNPs/MBA films were exposed to Cu^{2+} ion solution and left for 2 h at room temperature. After that, the samples were rinsed with water and dried under a vacuum. The shift in the λ_{max} for the SPR absorbance signal was measured by recording the UV/Vis absorbance spectra of the PP-PEI-AgNPs/MBA films exposed to the different concentrations of Cu^{2+} ions. To investigate the specificity of PP-PEI-AgNPs/MBA films toward Cu^{2+} ions, PP-PEI-AgNPs/MBA films were separately exposed to the aqueous solutions (1 mM) of different metal ions including Na^+ , K^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} , and Co^{2+} and the shifts in λ_{max} for the SPR absorbance signal were recorded.

2.6. H_2S Sensing. A stock solution of NaSH (aqueous 100 mM) was used to prepare the standard solutions of NaSH with 50 mM, 1 mM, 85 μM , 50 μM , 40 μM , 20 μM , 10 μM , 5 μM , and 1 μM concentrations. The PP-PEI-AgNPs-modified films were exposed to NaSH solution and left for 1.5 h at room temperature under orbital shaking. After that, the samples were rinsed with water and dried under a vacuum, and their SPR absorbance profiles were recorded.

2.7. Instrumentation. Bruker Alpha Platinum ATR-FTIR instrument (Alpha Bruker, Germany) operating from 4000–500 cm^{-1} was used to record FTIR spectra. Static water contact angles were recorded on a drop shape analyzer system (DSA30). UV printing was performed in a UV Irradiation chamber BS-03 (Mercury lamp (power 15 W), total lamps: 20, λ_{lamp} 352 nm) from Sankyo Denki, Japan. X-ray photoelectron spectroscopy (XPS) for elemental compositions and bonding information was performed using a Thermo Scientific K-Alpha. The $\text{Mg K}\alpha$ (1486.6 eV) X-ray source was operated at 300 W. The survey scans were carried out with a pass energy of 117.40 eV. The spectra were recorded using a 60° take-off angle relative to the surface normal. A Nova NanoSEM 450 was used to perform scanning electron microscopy (SEM). The optical properties of AgNPs-functionalized films were monitored by UV–Vis/NIR spectrophotometer (Jasco V-880) equipped with a halogen/deuterium lamp.

3. RESULTS AND DISCUSSION

Surface-confined growth of AgNPs was demonstrated on the surfaces of three chemically diverse polymer film substrates, namely, PP, PVC, and PET. Scheme 1A presents the illustration of the strategy that was employed for the surface chemical modification of polymeric film substrates. The first step of the surface modification involved exposing polymeric film substrates to UVO. The UVO surface treatment is known

to oxidize surfaces and introduces oxygen-containing functional groups on the surface.^{54,55} The UVO-treated surfaces were subjected to the process of silanization employing TMSPA to introduce acrylate groups at the surface of polymer film substrates. TMSPA-functionalized polymer film substrates were subjected to UV-printing using a UV curable coating consisting of an ICEMA monomer offering pendant isocyanate groups, a TMPTA triacrylate cross-linker, and an IRG 184 photoinitiator. The choice of ICEMA monomer during UV-printing resulted in the functionalization of polymer film substrates with a thin layer of UV-printed coating, displaying reactive isocyanate groups on their surfaces that could be employed in the subsequent derivatizations. The surface isocyanate groups were used to covalently conjugate PEI on the surface of UV-printed polymer film substrates through the facile base-catalyzed isocyanate/amine conjugation, resulting in the covalent bonding of PEI to the surface via urea linkage. PEI is known for its ability to simultaneously chelate and reduce metal ions and stabilize the resulting NPs.^{47,52,56} Capitalizing on this capacity of PEI, the surface-functionalized PEI was employed to trigger surface-confined growth of AgNPs. The surface-confined growth of AgNPs was carried out by three different approaches. In the first approach, PEI-functionalized polymer film surfaces were exposed to the aqueous AgNO_3 solution, as a precursor for the silver ions, without the aid of any additional externally added reducing agent, and surface-confined growth of AgNPs was monitored via SEM imaging. In the second approach, NaBH_4 was used as an additional reducing agent wherein the PEI-functionalized polymer film substrates were exposed to an aqueous solution containing both AgNO_3 and NaBH_4 . In the third approach, PEI-functionalized polymer film surfaces were first exposed to the aqueous AgNO_3 solution followed by blotting the surface to remove the AgNO_3 solution and exposing the surface to aqueous NaBH_4 solution. All three approaches to surface-confined growth of AgNPs were executed at room temperature. Besides amines, carboxylic acids have also been frequently employed as chelating, reducing, and stabilizing agents during the synthesis of NPs.^{16,57} In order to reveal the potential of surface-immobilized carboxylic acid groups for the surface-confined growth of AgNPs, PAA was covalently conjugated to the surface isocyanate groups through *N*-carboxylated anhydride linkage, which forms as a result of the reaction of isocyanate and COOH groups (Scheme 1A). In the same vein, we extended the range of surface functionalities and extended our exploration to include surface cationic groups in the form of quaternary amines to assess their ability to support surface-confined growth of AgNPs. To accomplish this, CC was reacted with the surface isocyanate groups through the alcohol group of CC that results in the immobilization of CC to the UV-printed surface via urethane linkage (Scheme 1A). While PEI was functionalized on the surface of all the UV-printed polymer film substrates (PP, PVC, and PET), the functionalization with PAA and CC was carried out as a proof of concept only on the surface of the UV-printed PP film.

The mechanical stability of UV-printed coatings was demonstrated by subjecting the UV-printed polymer film substrates to a tape test. An inspection of the UV-printed coatings before and after the tape test suggests that the coatings on the three polymer film substrates remained fully intact during the tape test (Figure S1). The mechanical robustness of the UV-printed coatings was further ascertained by SEM imaging (Figure S2) performed before (Figure

Figure 1. (a–c) C 1s high-resolution XPS scans of polymer films subjected to UV-printing employing ICEMA as a functional monomer and (d–f) their corresponding N 1s high-resolution XPS scans. (g–i) C 1s high-resolution XPS scans of UV-printed ICEMA-functionalized films after functionalization with PEI and (j–l) their corresponding N 1s high-resolution scans.

S2a,e,i,b,f,j) and after (Figure S2c,g,k,d,h,l) the tape test. A comparison of the surface (Figure S2a,e,i,c,g,k) and cross-sectional (Figure S2b,f,j,d,h,l) SEM images of UV-printed polymer films subjected to the tape test did not show any noticeable structural variations, highlighting the mechanical robustness of the UV-printed coating on all three chemically distinct flexible polymer film substrates.

After demonstrating the chemical robustness, the changes in the surface chemistry of polymer film substrates subjected to the UV-printing process depicted in Scheme 1 were monitored by FTIR spectroscopy (Figure S3 and Table S1). Figure S3a displays the FTIR spectra of pristine polymer film substrates where characteristic absorption bands for PP, PVC, and PET are highlighted. The FTIR spectra of pristine PP, PVC, and PET showed absorption bands centered at around 2923 cm⁻¹

that can be attributed to the C–H stretching vibrations. The absorbance bands corresponding to the bending vibrations of CH₂ and CH₃ groups in the case of PP were observed to appear at 1365 and 1453 cm⁻¹, respectively. Besides bending, rocking, and wagging vibrations for the aliphatic (CH₂ and CH) backbone of PVC appearing at 1425, 1324, 1240, and 958 cm⁻¹, the characteristic C–Cl stretching vibration was observed at 613 cm⁻¹ in the FTIR spectrum of pristine PVC. The FTIR spectrum of pristine PET films revealed absorbances characteristic of the carbonyl of ester linkage at 1707 cm⁻¹ and stretching vibration of the aromatic C=C bond at 1408 cm⁻¹ as well as absorbances at 1240 and 1085 cm⁻¹ that could be attributed to the stretching vibration of the C–O bond of the ester linkage. The strong absorbance signal observed at 720 cm⁻¹ in the FTIR spectrum of PET could be

attributed to the C–H bending vibration of the aromatic ring and the interaction of ester linkage and the aromatic ring present in PET. The FTIR spectra of UVO-treated and TMSPA-functionalized polymer film substrates revealed no additional peaks compared to the FTIR spectra of the pristine substrates (Figure S3b). This can be due to the fact that the sample depth that is probed during the FTIR analysis in ATR mode is in several microns, while the surface chemical modifications through UVO treatment and TMSPA functionalization are restricted to a few molecular layers on the surface of a substrate. The FTIR analysis of the UV-printed polymer film substrates revealed absorbances characteristic of the chemical nature of the UV-printed coating on the surface of polymer film substrates (Figure S3c). The FTIR spectra of all the UV-printed polymer film substrates showed identical absorbances, suggesting an effective functionalization of all the substrates and their identical surface chemistry despite their distinct bulk chemical natures. The absorbance at 2260 cm^{-1} appearing in the FTIR spectra of all the UV-printed polymer film substrates corresponds to the isocyanate groups (–NCO) of the UV-printed coating. The other common absorbance prominent in the FTIR spectra of all the UV-printed polymer film substrates appeared at 1720 cm^{-1} that corresponds to the ester linkages of the ICEMA monomer and TMPTA cross-linker used during the UV-printing process. The conjugation of surface isocyanate groups with PEI, PAA, and CC was ascertained by the disappearance of the characteristic absorbance peak for –NCO groups (Figure S3).

The evolution of the surface chemical nature of all the polymer film substrates as a result of the surface functionalization depicted in Scheme 1 was followed by measuring the surface water contact angles (WCAs). As shown in Figure S4, the static water contact angles of pristine PP, PVC, and PET were around $99^\circ \pm 1$, $83^\circ \pm 2$, and $86^\circ \pm 2$, respectively. After UVO treatment, the WCAs for PP, PVC, and PET dropped to $70^\circ \pm 2$, $66^\circ \pm 2$, and $68^\circ \pm 2$, respectively. This increase in hydrophilicity can be associated with the introduction of hydrophilic moieties on the surface as a result of the surface oxidation of polymer film substrates upon UVO treatment. The functionalization of UVO-treated substrates with TMSPA led to an increase in the WCAs for all the substrates. The WCAs of TMSPA-functionalized PP, PVC, and PET polymer film substrates were observed to around 84, 83, and 86° , respectively. The approximately similar water contact angles after TMSPA functionalization can stem from the identical surface chemistry of polymer film substrates displaying acrylate groups on their surfaces. Owing to their identical surface chemistries, the UV-printed polymer film substrates also displayed almost identical WCAs (78° for PP and PVC and 80° for PET). The WCAs of all the UV-printed polymer film substrates were observed to decrease to almost the same extent (57° for PP and 59° for PVC and PET) after covalent conjugation of PEI to the surface isocyanate groups. The lower WCAs of PEI-functionalized polymer film substrates corroborate the successful incorporation of hydrophilic amino groups to the surface of all the polymer film substrates. The identical WCAs of chemically different PP, PVC, and PET substrates at the stages of TMSPA functionalization, UV-printing, and PEI functionalization suggest identical surface chemistries despite the markedly distinct bulk chemical nature of the respective polymer film substrates. Conjugation of surface isocyanate groups of PP-ICEMA with CC and PAA led to an increase in the surface hydrophilicity. Due to the incorporation of

quaternary amine groups on the surface, the PP-CC surface displayed a WCA of around 66° . The surface WCA for the PP-PAA substrate was around 67° , 65° , and 50° , respectively, under acidic, neutral, and basic pH conditions, which corresponds to the different states of protonation under different pH conditions.

In addition to FTIR spectroscopy and WCA measurement, XPS analysis (Figure 1) was performed to characterize the changes in the surface chemistry of polymer film substrates that were subjected to the surface functionalization depicted in Scheme 1. The high-resolution C 1s XPS scans for pristine polymer film substrates are depicted in Figure S5. In the case of pristine PP, the C 1s scan revealed a single peak (284.78 eV) corresponding to the carbon atoms in aliphatic C–C and C–H bonds. The C 1s scan of pristine PVC could be deconvoluted into the characteristic peaks for carbon atoms in aliphatic C–C and C–H (284.7 eV) and C–Cl (285.94 eV) bonds. A minor signal matching the position of carbon atoms in carbonyl (287.6 eV) groups was also observed in the C 1s scan of PVC. This signal may be attributed to the ester groups containing plasticizers that are used in the manufacturing of PVC films. Besides the C 1s high-resolution scan, the Cl 2p high-resolution scan was also recorded for the pristine PVC film. The Cl 2p high-resolution scan of pristine PVC could be curve fitted by the component signals stemming from Cl $2p_{3/2}$ (199.4 eV) and Cl $2p_{1/2}$ (201 eV). A minor signal (197.20 eV) appearing in the Cl 2p scan of PVC could be attributed to the radical anion of the chloromethyl group formed during X-ray excitation in the XPS analysis chamber.⁵⁸ The C 1s high-resolution scan for the pristine PET substrate consisted of component peaks corresponding to the carbon atoms in aliphatic C–C, C–H (284.73 eV), C–O (286.3 eV), and O–C=O (288.75 eV) bonds. The XPS analyses of pristine polymer film substrates nicely corresponded to their respective chemical natures. The UVO treatment of pristine polymer films was expected to install oxygen-bearing functionalities on their surfaces. The incorporation of oxygen-bearing functionalities on the surface of UVO-treated PP films (PP-UVO) led to the appearance of a small signal in the C 1s scan corresponding to the carbon atom (285.7 eV) bonded to oxygen (Figure S6a). The presence of signals for the carbon atoms bonded to oxygen species in the C 1s scans of pristine PVC and PET (Figure S5b,d) masked the observation of any additional signals that could be attributed to the UVO treatment of these substrates (Figure S6b,c). However, an increase in the ratio of atomic percentages of oxygen and carbon (O/C) in the case of UVO-treated PVC (PVC-UVO) and PET (PET-UVO) compared to the O/C ratio for pristine substrates supported the incorporation of oxygen-containing species on the surfaces of PVC and PET upon exposure to UVO (Table S3). The functionalization of UVO-treated polymer film substrates with TMSPA resulted in the appearance of the characteristic signal for the Si atom in the Si 2p high-resolution scans of all the TMSPA-functionalized substrates. Si 2p signals appeared at 102.58 eV for PP-TMSPA, 102.06 eV for PVC-TMSPA, and 99.8 eV for PET-TMSPA (Figure S6g–i). It is worthwhile mentioning here that the films used in this study were obtained from the industries where silica-containing additives might have added in the films, which sometimes resulted in the appearance of signals for silicon in the XPS analysis of pristine substrates. Following the surface functionalization with TMSPA, all the polymer film substrates were subjected to UV-printing employing ICEMA as a reactive

Figure 2. SEM images revealing the time-dependent surface-confined growth of AgNPs on the surface of PP-PEI films without the addition of an external reducing agent. Images taken at different time points for exposure of the PP-PEI surface to the AgNPs precursor solution and corresponding particle size and size distribution are depicted: (a–c) 30 min, (d–f) 60 min, (g–i) 90 min, (j–l) 120 min, (m–o) 150 min, and (p–r) 180 min.

monomer. It is worthwhile mentioning here that the survey scans (Figure S8) and C 1s and N 1s high-resolution XPS scans of the three chemically distinct polymer film substrates were identical (Figure 1a–f), which corresponds to their identical surface chemistry despite their markedly different bulk chemical nature. The C 1s high-resolution scan of all the UV-printed polymer film substrates could be deconvoluted into three components that can be attributed to carbon atoms

in aliphatic C–C, C–H bonds, carbon atoms in C–O, C–N bonds, and carbon atoms in the carbonyl group (ester and isocyanate) (Figure 1a–c). Furthermore, the N 1s high-resolution scans (Figure 1d–f) of all the UV-printed polymer film substrates showed a single peak characteristic of the nitrogen atom (C–N) at around 399.3 eV stemming from the isocyanate groups of the ICEMA monomer incorporated on the surface of all the UV-printed polymer film substrates. The

Figure 3. SEM images revealing the time-dependent surface-confined growth of AgNPs on the surface of PP-PEI films using NaBH_4 as an external reducing agent in the presence of the precursor for AgNPs. Images taken at different time points: (a and b) 90 min and (d and e) 120 min. Particle size and size distribution are also depicted for (c) 90 min and (f) 120 min exposure times.

reaction of isocyanate groups of the UV-printed ICEMA-containing coatings with the amino groups of PEI resulted in the fabrication of PEI-functionalized polymer film substrates (PP-PEI, PVC-PEI, and PET-PEI). Due to their identical surface chemistry, the C 1s and N 1s high-resolution XPS scans of all functionalized polymer film substrates showed identical patterns. The C 1s high-resolution XPS scan consisted of component peaks corresponding to the carbon atoms in the aliphatic C–C, C–H bonds (284.73 eV), C–N/C–O bond (285.8 eV), and carbonyl group (288 eV) (Figure 1g–i). Meanwhile, the N 1s high-resolution XPS scans of all functionalized polymer film substrates could be deconvoluted into constituting peaks corresponding to C–NH₂ (398.69 eV), C–NH–C (399.5 eV), and N–(C)₃ (401 eV) binding arrangements (Figure 1j–l). Similarly, in the case of covalent conjugation of surface isocyanate groups with the CC (Figure S7a), the C 1s high-resolution scan could be deconvoluted into the aliphatic C–C, C–H bonds (284.6 eV), C–N/C–O bond (285.9 eV), and carbonyl group (288.38 eV). A distinct signal for the quaternary amine (401.08 eV) and its Cl (Cl 3p_{1/2} and Cl 3p_{3/2} at 199.4 and 197.7 eV, respectively) counterion could be clearly observed in N 1s and Cl 3p high-resolution scans of PP-CC (Figure S7b,c), which confirmed the successful surface functionalization with quaternary amine-bearing choline chloride. The C 1s high-resolution scan of PP-PAA (Figure S7d) showed a higher intensity of the signal for C–O corroborating the surface functionalization with PAA. The relative percentages of each component peak in the C 1s high-resolution scans of all the substrates at all stages of modification are depicted in Table S4.

Having demonstrated the applicability and versatility of our UV-printing strategy for the functionalization of chemically diverse substrates, we employed the surface-immobilized PEI to achieve a surface-confined growth of AgNPs on the surface of PEI-functionalized polymer film substrates. The process optimization for the surface-confined growth of AgNPs was performed on the surface of PP-PEI, and the optimized protocol was applied to grow AgNPs on the surface of PVC-

PEI and PET-PEI. Three approaches were applied during the optimization of the surface-confined growth of AgNPs. The first approach capitalized on the ability of the surface-immobilized PEI to function as a chelating, reducing, and stabilizing agent and involved placing aqueous solution of the AgNPs precursor (AgNO_3) on the surface of PP-PEI for a predefined period. The precursor solution was then blotted, and films were thoroughly washed with DI water. No external reducing agent was added in the first approach, and surface-confined growth of AgNPs was monitored by SEM imaging of the PP-PEI surfaces exposed to AgNO_3 solution for different time intervals (Figure 2). The color of PP-PEI films changed from colorless to light yellow upon exposure to the AgNO_3 solution, and AgNPs were clearly observed to emerge on the surface of PP-PEI after 30 min of exposure to AgNO_3 solution (Figure 2a,b). The average size of AgNPs at 30 min exposure time was found to be around 55 (± 10) nm (Figure 2c). With the increase in exposure time of the PP-PEI surface to AgNO_3 solution, the number of AgNPs (particle density) on the surface of PP-PEI was observed to gradually increase, while at the same time, the size of the AgNPs was observed to decrease. The particles appearing on the surface of PP-PEI after 60 min were around 45 (± 7) nm. At 90 min exposure, the particle size was observed to decrease to 38 (± 7) nm and the size was observed to further decrease to 28 (± 5) nm at 150 min exposure time. Even smaller-sized particles were observed at 180 min exposure time where the particle size was found to have decreased to 15 (± 2) nm. The PP-PEI surface exposed to the AgNO_3 solution for 180 min, the longest exposure time employed in this study, was densely covered by the small-sized AgNPs. At the longer exposure time, the observed growth of smaller particles at the expense of larger particles can be explained by the “digestive ripening” hypothesis for NPs nucleation and growth, which suggests that during the synthesis of NPs, larger particles can redissolve, favoring the growth of smaller NPs.⁵⁹

In our second approach, the effect of the addition of sodium borohydride (NaBH_4) as an external reducing agent was

Figure 4. SEM images revealing the time-dependent surface-confined growth of AgNPs on the surface of PP-PEI films sequentially exposed to the solutions of the AgNPs precursor with NaBH_4 as an external reducing agent: Total exposure times: (a and b) 90 min, (d and e) 120 min, (g and h) 150 min, and (j and k) 180 min. (c, f, i, and l) Corresponding particle size and size distribution.

investigated. In this approach, AgNO_3 solution was placed on the surface of PP-PEI for 1 h followed by the addition of NaBH_4 solution into the AgNO_3 solution covering the PP-PEI surface. The precursor solution was found to turn grayish in color upon the addition of NaBH_4 solution. The growth of AgNPs was monitored by SEM imaging, the surface exposed to the solutions of AgNO_3 for 1 h followed by the addition of NaBH_4 solution in the AgNO_3 solution and recovering the films at different time intervals after addition of NaBH_4 (Figure 3). It can be seen from the SEM images that the addition of NaBH_4 as a co-reducing agent in the solution in contact with the PP-PEI surface results in the formation of larger particles (78 ± 31 nm) at 90 min total exposure time (1 h exposure to AgNO_3 solution and 30 min after addition of NaBH_4 solution) when compared to the particles (38 ± 7 nm) formed in the first approach at the equivalent exposure time. Besides the formation of larger particles in the second approach, the size distribution was also extremely broad when compared to the

relatively narrow size distribution of the particles observed in the first approach. Extending the total exposure time to 120 min in the case of the second approach led to almost identical results. Inferring from the larger particle size, significantly broader size distribution, and higher density of particles per unit area (Figure S9b) in the case of the second approach, the addition of NaBH_4 in the AgNO_3 solution results in uncontrolled growth of AgNPs, presumably due to the NaBH_4 -triggered increase in the rate of reduction of silver ions in the solution in contact with the surface and subsequent assembly of reduced ions into larger AgNPs.

Our third approach referred to as the sequential exposure approach involved a 1 h exposure of the PP-PEI surface to the AgNO_3 solution, after which the precursor solution was removed from the surface of PP-PEI via blotting. The blotted PP-PEI surface was then exposed to the solution of NaBH_4 as the external reducing agent. The growth of AgNPs as a result of the exposure of the PP-PEI surfaces to AgNO_3 and NaBH_4

Figure 5. SEM images of AgNPs confined on the surfaces of (a and b) PP-CC and (g and h) PP-PAA via the first approach and SEM images of AgNPs grown on the surface of (d and e) PP-CC and (j and k) PP-PAA via the third approach. (c, f, i, and l) Corresponding particle size and size distribution.

solutions in a sequential manner was monitored via SEM imaging at different total exposure times (Figure 4). The SEM images at 90 min total exposure time revealed that the sequential exposure approach resulted in the formation of AgNPs on the surface of PP-PEI, which were comparable in size but greater in number when compared to the AgNPs formed on the surface of PP-PEI in the first approach where no external reducing agent was added. This suggests that the use of an external reducing agent increases the rate of particle growth, which was also observed in our second approach. In addition, the AgNPs formed during the sequential approach showed relatively smaller size, narrower size distribution, lesser clustering, and uniform surface coverage compared to the AgNPs formed on the surface of PP-PEI during the second approach at the equivalent total exposure times. As with the first approach, the size of the AgNPs was observed to decrease with the increase in exposure time. An exposure time of 150 min was found to result in small-sized AgNPs uniformly

covering the entire surface and was identified as the optimum exposure time. Extending the exposure time to 180 min resulted in the appearance of relatively larger AgNPs. We believe that after covering the available surface area with smaller-sized particles, the particles start to agglomerate and cluster on the surface of smaller-sized particles. Comparing the results obtained for the growth of AgNPs on the surface of PP-PEI, it can be concluded that the first approach is a suitable method for applications where low surface density of NPs is desirable while the third so-called sequential approach is suitable for applications where higher surface density of NPs is needed. In addition, in both the first and third approaches, a total exposure time of 150 min was found to result in surfaces uniformly decorated with AgNPs. The total exposure time of 150 min was employed in all the subsequent experiments performed in this study. A comparison of the particle density per unit area estimated from ImageJ is provided in Figure S9 in the SI.

Figure 6. UV/Vis absorption spectra of PP-AgNPs fabricated by the (a) first (no external reducing agent) and (b) third (with an external reducing agent) approach at different reaction times. UV/Vis absorption spectra of (c) PP-CC-AgNPs, PP-PAA-AgNPs, and PP-PEI-AgNPs developed by the first approach and (d) PP-CC-AgNPs, PP-PAA-AgNPs, and PP-PEI-AgNPs developed by the third approach.

In order to understand the role of surface chemistry in the growth of AgNPs, we subjected PP-CC and PP-PAA polymer film substrates to the first and third approaches for surface-confined growth of AgNPs. In these proof-of-concept experiments, PP-CC offers surface quaternary amine groups while PP-PAA displays carboxylic acid groups on its surface. SEM images of both surfaces subjected to AgNPs growth by the first and third approaches are depicted in Figure 5. In the case of PP-CC subjected to AgNPs growth by the first approach, the film surface was functionalized with few but large particles with a wide size range and low surface density. In contrast, the SEM images of the surface of PP-CC subjected to AgNPs growth via the third approach revealed surface functionalization with small particles (Figure 5d,e). The surface of PP-PAA interestingly showed growth of particles with two clearly distinct size distributions when subjected to the first approach. The growth of AgNPs on PP-PAA via the third approach led to a surface-functionalized with small-sized AgNPs with uniform size distribution. The origin of larger particles on the surfaces of PP-CC and PP-PAA during the particle growth via the first approach is unclear; however, the smaller particles observed in the case of PP-PAA could emerge from the ability of carboxylic acids to act as a reducing agent. Irrespective of the surface chemical nature, the third approach where NaBH_4 is applied as an external catalyst in a sequential manner decorated the surfaces with small particles with narrow size distribution.

Besides SEM imaging, formation of AgNPs on the surface of PP-PEI was also characterized by UV/Vis spectroscopy. The UV/Vis absorption spectra of AgNPs are known to show characteristic absorbance between 400 and 530 nm due to the localized SPR signal of AgNPs. The exact wavelength of absorbance maximum (λ_{max}) depends on the size and shape of the AgNPs, their state of aggregation, and the chemical nature of the surrounding environment. The absorbance for the smaller-sized AgNPs appears at a relatively shorter wavelength when compared with the larger-sized AgNPs. The UV/Vis

absorbance spectra of the PP-PEI subjected to the growth of AgNPs through the first and third approaches are depicted in Figure 6. The absorbance band due to the SPR of surface-confined AgNPs was found to appear in the UV/Vis spectra of all the PP-AgNPs polymer film substrates. Complementing the observation of decrease in the particle size of the AgNPs formed on the surface of PP-PEI with an increase in the exposure time during the first approach (Figure 2), the λ_{max} for the SPR absorbance band was observed to start shifting to the shorter wavelengths as the exposure time was increased beyond 120 min (Figure 6a). The λ_{max} for the SPR absorbance band in the UV/Vis absorbance spectra of PP-PEI-AgNPs fabricated via the third approach (sequential approach) did not show much variation with the increase in exposure time (Figure 6b). The SPR absorbance λ_{max} was observed to shift to a slightly smaller wavelength at 120 and 150 min exposure times, which corroborates the observed decrease in the particle size in the SEM analysis (Figure 4). Increasing the exposure time to 180 min led to a slight increase in the SPR absorbance λ_{max} , which is also in line with the increase in particle size observed in the SEM analysis (Figure 4). It is worth while mentioning here that a significantly higher intensity of the SPR absorbance was observed for the PP-PEI surfaces subjected to surface-confined growth of AgNPs via the third approach. By relating the absorbance intensity of the SPR band to the number of particles grown on the surface, it can be inferred that the use of NaBH_4 as an external reducing agent in the sequential approach led to the surfaces with a higher number of particles grown on their surfaces. This also complements the relatively higher particle density observed in the case of PP-PEI surfaces functionalized with AgNPs via the sequential approach as compared to the PP-PEI surfaces functionalized with AgNPs via the first approach. This again suggests that the third approach results in the formation of a higher number of small-sized particles with narrow size distribution.

Figure 7. (a) Comparison of specificity based on the extent of the $\lambda_{\max}$ shift of SPR absorption maxima of 4-MBA-functionalized PP-PEI-AgNPs films exposed to different metal ions. (b) Extent of the $\lambda_{\max}$ shift for SPR peaks observed in the UV/Vis absorption spectra of PP-PEI-AgNPs-MBA films exposed to aqueous solutions containing different concentrations of Cu²⁺ ions. (The solid line shall guide the eye).

The absorption bands due to the SPR of the surface-confined AgNPs grown on the surface of PP-CC and PP-PAA by the first and third approaches at a total exposure time of 150 min are depicted in Figure 6c,d. For comparison, the SPR bands for AgNPs grown on the surface of PP-PEI via the first and third approaches at equivalent total exposure times are also presented. It is evident from Figure 6c that the intensity of SPR absorbance bands for AgNPs-functionalized PP-CC and PP-PAA film substrates developed through the first approach are even lower than the intensity of the SPR absorbance noted for the AgNPs-functionalized PP-PEI developed under the same conditions. The intensities of SPR absorbance bands for the PP-CC and PP-PAA surfaces functionalized with AgNPs through the third approach were slightly higher than the intensities of the SPR absorbance bands noted for these substrates upon functionalization via the first approach. This suggests that the addition of NaBH₄ as an external reducing agent resulted in a slight increase in the number of AgNPs on the surfaces of PP-CC and PP-PAA. The highest intensity of the SPR absorbance band was observed for the PP-PEI polymer film substrates functionalized with AgNPs via the third approach. We attribute this observation to the relatively stronger metal ion chelating ability of amine groups present in PEI, compared to the other functionalities employed in this study, which led to an uptake of a relatively higher number of silver ions. The higher number of silver ions impregnated on the surface of PP-PEI consequently resulted in the formation of a higher number of AgNPs upon subsequent exposure to NaBH₄ as an external reducing agent.

The growth of AgNPs on the surface of UV-printed polymer film substrates imparted light yellow color to these films. The strength of the color as observed by the naked eye corresponds to the intensity of the SPR bands observed in the UV/Vis absorbance spectra. As can be seen in Figure S12, the films subjected to the surface-confined growth of AgNPs via the third approach appeared sharper in color as compared to the films where AgNPs were grown via the first approach. Corroborating the trend observed for the intensities of the SPR bands in the UV/Vis absorbance spectra (Figure 6), PP-PEI-AgNPs films developed through the third approach showed the strongest color.

Because of the higher surface density of AgNPs and the highest intensity of the SPR absorbance band observed in the case of particles grown via the third approach, this sequential exposure approach at 150 min exposure time was applied to grow AgNPs on the surface of PVC-PEI and PET-PEI polymer

film substrates. The SEM images (Figure S13) of PVC-PEI and PET-PEI subjected to the sequential exposure approach showed that both the surfaces were fully covered with AgNPs. Besides UV/Vis spectroscopic analysis and SEM imaging, the AgNPs-functionalized surfaces were also characterized by XPS. The XPS survey scans revealed the presence of silver on the surface of all the films fabricated by different methods. The Ag 3d high-resolution XPS scans are depicted in Figure S11, clearly revealing the presence of Ag on all the AgNPs-functionalized polymer film substrates. The high-resolution Ag 3d XPS scans for all the substrates were nicely deconvoluted into two distinct peaks corresponding to Ag 3d_{5/2} (368 eV) and Ag 3d_{3/2} (374 eV).⁶⁰ The appearance of peaks at these binding energies and splitting of 3d doublet of Ag indicated the presence of AgNPs in the Ag⁰ state. The XPS analysis corroborates that the sequential exposure approach can be conveniently applied to grow AgNPs on the surface of three chemically distinct polymer film substrates.

The developed AgNPs-functionalized flexible polymer film substrates were employed as a chemosensor for Cu²⁺ and H₂S sensing (Scheme 1B).

3.1. Cu²⁺ Ion Sensing. The SPR phenomenon exhibited by the metal NPs is known to sensitively respond to the interaction of various chemical species with the metal surface. Surface functionalization of the SPR-exhibiting materials with ligands that can specifically bind to an analyte can predictively manifest as a change in the wavelength of the SPR resonant peak, which offers an attractive platform for developing a variety of physical, chemical, and biosensors.⁶¹ The SPR phenomenon exhibited by the surface-confined AgNPs developed in this study was exploited to develop a sensing platform for Cu²⁺ ions. The AgNPs confined on the surface of PP-PEI-AgNPs film were first functionalized with 4-MBA as a ligand to interact with the ions in an aqueous environment. The functionalization of the PP-PEI-AgNPs film substrate with 4-MBA led to the appearance of a characteristic signal for sulfur in the XPS analysis (Figure S14). The high-resolution S 2p scan could be curve fitted for S 2p_{3/2} and S 2p_{1/2} signals.^{62,63} The main component S 2p_{3/2} at 162 eV can be attributed to the Ag-thiolate bond. The minor component S 2p_{1/2} at 163 eV can be assigned to unbound free thiol groups.

The UV/Vis absorption spectra for PP-PEI-AgNPs before and after functionalization with 4-MBA are depicted in Figure S15. The $\lambda_{\max}$ for SPR absorbance was observed to shift to longer wavelengths after functionalization with 4-MBA. The choice of 4-MBA as a metal ion receptor was based on its

Figure 8. (a–f) UV/Vis absorbance spectra obtained before and after exposure to different concentrations of NaSH for H₂S sensing, (g) visual decolorization of PP-PEI-AgNPs films upon exposure to the solutions containing different concentrations of NaSH, and (h) high-resolution XPS scan of the PP-PEI-AgNPs film treated with 50 μmol NaSH solution.

strong affinity for silver surfaces via its mercapto group and its ability to coordinate with ions via the carboxyl group (–COOH). In order to demonstrate the sensitivity and specificity of the PP-PEI-AgNPs/MBA polymer film substrates as an ion sensor, the films were separately immersed for 2 h in the aqueous solutions containing K⁺, Na⁺, Ni²⁺, Zn²⁺, Co²⁺, Pb²⁺, and Cu²⁺ at 1 mM concentration and room temperature. A shift in the wavelength of the $\lambda_{\max}$ for the SPR resonant peak was monitored by recording the UV/Vis absorbance of the PP-PEI-AgNPs/MBA after exposure to the solutions of different ions. As shown in Figure 7a, a clear shift in the wavelength was observed upon exposing the PP-PEI-AgNPs/MBA sensor film to Cu²⁺, while no noticeable change was observed when the sensor film was brought in contact with other cations. These results highlight that the developed PP-PEI-AgNPs/MBA film as an ion sensor was specifically sensitive toward Cu²⁺. The observed specificity of the proposed sensor toward Cu²⁺ could be due to stronger coordination of Cu²⁺ with the carboxyl group of 4-MBA immobilized on the surface of the PP-PEI-AgNPs/MBA polymer film substrate. The sensitivity of the sensor toward detection of Cu²⁺ ions was studied by exposing the PP-PEI-AgNPs/MBA polymer film substrate to solutions containing different concentrations of Cu²⁺ ions and monitoring the change in $\lambda_{\max}$ for the SPR resonant peak by recording UV/Vis spectra. The corresponding SPR absorbance profiles of PP-PEI-AgNPs, PP-PEI-AgNPs/MBA, and PP-PEI-AgNPs/MBA after exposure to Cu ions at different concentrations are depicted in Figure S15. The plot of wavelength shift (nm) of the SPR resonant peak as a function

of Cu²⁺ concentration revealed a clearly noticeable response in the concentration range from 1 to 100 ppm. The limit of detection (LOD) for Cu²⁺ ions was calculated by using the following equation:⁶⁴

$$\text{limit of detection} = \frac{3\sigma}{K}$$

where σ is the standard deviation in the position of the $\lambda_{\max}$ for the SPR resonant peak observed in the UV/Vis absorbance spectra of blank samples (PP-PEI-AgNPs/MBA before exposure to Cu²⁺ ions). To obtain values for σ , the $\lambda_{\max}$ values for the SPR absorbances of blank samples were recorded for six different samples. K is the slope of the wavelength shift versus $\ln$ Cu²⁺ ion concentration ranging from 1 to 100 ppm (Figure S16).⁶⁵ The data obtained from this equation suggests that the PP-PEI-AgNPs/MBA film substrate could reliably detect Cu²⁺ ions at a concentration as low as 2.6 ppm.

We also assessed the effect of pH on Cu²⁺ ions in the pH range 2–12. It is pertinent to mention here that Cu²⁺ converts into insoluble copper hydroxide in the presence of hydroxide ions originating from sodium hydroxide (NaOH) that was used to achieve basic pH.⁶⁶ The precipitation of copper hydroxide deprives the solution of Cu²⁺ ions. All the solutions where we maintained the pH values of 6, 8, 10, and 12 using NaOH resulted in the formation of precipitates, and no sensor response was observed at these pH values. On the other hand, the solutions remained clear at acidic pH values (2 and 4) and clear shifts in the wavelength of the $\lambda_{\max}$ for SPR resonant peaks were observed (Figure S17). It is worthwhile mentioning

that the intrinsic pH of copper chloride solution without adding any acid or base was around 4–5. This implies that the copper chloride solution is inherently acidic, and all the reported data are collected at slightly acidic pH.

Besides Cu^{2+} ions, the PP-PEI-AgNPs film substrates were also employed as a H_2S sensing platform. NaSH, a half neutralized derivative of H_2S , was used as a H_2S donor. Contrary to Cu^{2+} ion sensing where the shift in the λ_{max} for the SPR absorbance was used as the reporting signal, the H_2S sensing was enabled by a reduction in the intensity of the SPR absorbance band upon exposure of the PP-PEI-AgNPs film to NaSH solution. A significant reduction in the intensity of the SPR absorbance band was observed when the PP-PEI-AgNPs film was exposed to 50 mM aqueous NaSH solution for 30 min. The SPR band was found to completely disappear when the exposure time was increased to 1.5 h (Figure S18). We also assessed the effect of pH on the change in the intensity of the SPR absorbance band upon exposure to NaSH solution at different pH values. Interestingly, the change in intensity was clearly visible at acidic pH and in the case of solutions where no external acid or base was added. However, the SPR signal was found to lose its sensitivity toward analytes and remained unchanged under basic pH conditions (Figure S19). We then exposed the PP-PEI-AgNPs film sensor to aqueous solutions containing different concentrations of NaSH to determine the sensitivity of the sensing platform. The UV/Vis absorbance spectra displaying the SPR absorbance bands of the PP-PEI-AgNPs film sensor before and after exposure to 1, 5, 20, 40, and 50 μM aqueous solutions of NaSH are depicted in Figure 8a–e. The SPR bands are presented as an average of three different measurements. It is evident from Figure 8a that the intensity of SPR bands decreased only slightly when the PP-PEI-AgNPs film sensor was exposed to 1 μM aqueous solutions of NaSH, and the percentage decrease was estimated to be around 4.8%. However, the intensity of the SPR band was found to decrease by 41.5% upon exposure to 5 μM aqueous solutions of NaSH. Further increasing the concentration and exposing the PP-PEI-AgNPs film sensor to 20 and 40 μM aqueous solutions of NaSH resulted in respective decreases of 62.8 and 74.3% in the intensity of SPR absorbance bands (Figure 8). A maximum decrease of 96.4% in the intensity of SPR bands was observed when the PP-PEI-AgNPs film sensor was exposed to 50 μM NaSH solution. It can be inferred from this data that the PP-PEI-AgNPs film sensor could sensitively respond to NaSH, a H_2S donor, in a concentration range of 5–50 μM . Besides the decrease in the absorbance intensity of SPR bands as monitored by UV/Vis spectroscopy, PP-PEI-AgNPs film sensors were observed to undergo a corresponding decolorization that could be observed by the naked eye (Figure 8g). An XPS analysis of the PP-PEI-AgNPs film sensor exposed to 50 μM NaSH solution revealed the presence of sulfur incorporated on the surface as a result of the interaction with NaSH (Figure 8h). The decrease in the intensity of the SPR absorbance band, visually observable decoloration, and observation of sulfur incorporated on the surface collectively suggest that the AgNPs on the surface of the PP-PEI-AgNPs film underwent a chemical reaction with the sulfide ions that may have transformed Ag^0 on the surface of AgNPs to the sulfide of silver (Ag_2S). Ag_2S formed on the surface of surface-confined AgNPs led to the disruption of the SPR that manifested in the decrease in the intensity of SPR absorbance bands and visual decoloration of the PP-PEI-AgNPs film. These results underline the potential of the PP-

PEI-AgNPs film for application as a colorimetric sensor for H_2S sensing.

4. CONCLUSIONS

In conclusion, employing a combination of UV-printing to install reactive ($-\text{NCO}$) surface functional groups for subsequent chemical modification with PEI and subsequent PEI-assisted surface-confined growth of AgNPs, we have demonstrated a substrate-independent strategy for surface-confined growth of AgNPs on the surfaces of chemically diverse flexible polymer film substrates (PP, PVC, and PET). After thorough optimization, sequential exposure of PEI-functionalized flexible film substrates to aqueous solutions containing Ag^+ ions and NaBH_4 was found to be an optimum approach to grow uniformly sized AgNPs with narrow size distribution. The amine group-bearing surface-confined PEI moieties were found to exhibit the superior potential to assist in the surface-confined growth of AgNPs compared to the surface-confined quaternary amine-bearing CC and carboxylic acid group-bearing PAA. We were able to exploit the sensitivity of SPR absorbance of the surface-confined AgNPs for chemical sensing of Cu^{2+} ions and H_2S . The Cu^{2+} ion sensing with a limit of detection of 2.6 ppm was enabled by a bathochromic shift in the λ_{max} for SPR absorbance of 4-MBA-functionalized surface-confined AgNPs upon exposure to an aqueous solution containing Cu^{2+} ions. The SPR absorbance of AgNPs confined on the surface of flexible PP films was found to diminish upon exposure to an aqueous solution of NaSH, which acts as a H_2S donor. The SPR absorbance intensity decreased more than 40% when AgNPs confined on the surface of flexible PP films were exposed to 5 μM aqueous solutions of NaSH. The SPR signal in the UV/Vis absorbance spectra as well as the distinct color of flexible PP films bearing surface-confined AgNPs completely vanished when the concentration of NaSH solution was increased to 50 μM . In short, we have developed a facile avenue to flexible polymer films with surface-confined AgNPs and have demonstrated the chemical sensing potential of these new materials. Since the developed strategy can be used to functionalize a wide range of flexible polymer substrates with a variety of chemically diverse metal NPs, this work has the potential to augment future developments in the application domains that rely on the surface-confined metal NPs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.1c01426>.

Demonstration of the tape test, a list of wavenumbers and corresponding functional groups, high-resolution C 1s XPS scans of pristine polymer films substrates, polymer films treated with UVO and functionalized with TMSPA, Si 2p high-resolution XPS scans of polymer films functionalized with TMSPA, a list of water contact angles and estimated percentages of different carbon components from C 1s high-resolution scans, percentages of surface C and O contents and O/C ratios of pristine and UVO-treated polymer film substrates, all XPS survey scans and corresponding surface atomic concentrations (%) of different elements, surface particle density data, high-resolution Ag 3d XPS scans, relative percentages of live and dead *Escherichia coli* and *Staphylococcus aureus*, S 2p XPS scan of PP-AgNPs

films functionalized with 4-MBA, UV/Vis absorbance plots displaying SPR of surface-confined AgNPs, UV/Vis absorbance plots demonstrating the effect of pH on Cu²⁺ and H₂S sensing, and effect of NaSH solution on the SPR absorbance of surface-confined AgNPs at 50 μM concentration (PDF)

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Notes

The authors declare no competing financial interest.

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