LANGMUIR

Integration of PEGylated Polyaniline Nanocoatings with Multiple Plastic Substrates Generates Comparable Antifouling Performance

Chen-Xi Shuai, Yuan He, Pei Su, Qiaoling Huang, Deng Pan, Qingchi Xu,* Danqing Feng,* and Yuan Jiang*



studies have made progress in delivering various conducting polymer thin films via oxidative chemical vapor deposition. Herein, Water flow **PEGylated** polyaniline we develop a solution-based approach to polyaniline (PANI) and nanocoating Anti-fouling property PEGylated PANI nanocoatings on multiple engineering plastics

followed by evaluating their antifouling performance. The procedure relies on the formation of uniform, lyotropic V_2O_5 nH_2O thin films on plastics assisted by a surfactant-sodium N-lauroylsarcosinate. Next, in situ, oxidative polymerization causes the formation of nanofibrous PANI nanocoatings. Finally, interfacial functionalization leads to PEGylated PANI nanocoatings, and the steric nanolayer effectively repels the adsorption of bovine serum albumin and the attachment of the bacterium Pseudoalteromonas sp. on the surface. It is worth noting that the antifouling properties rely mainly on the presence of PEGylated PANI nanocoatings, irrespective of the type of plastic substrates underneath. The current study therefore opens an avenue for the solution-based delivery of conducting polymer-based, functional nanocoatings on hydrophobic substrates in a controllable manner with the availability of further modification.

INTRODUCTION

Plastics are increasingly important materials used in the fabrication of biosensors, biomedical and marine equipment, food storage containers, water purification membranes, for example.¹⁻⁷ Conducting polymers exhibit intrinsic electric conductivity, tunable hydrophilicity, availability of chemical modification, chemical and mechanical stability, and biocompatibility, and their coupling with plastics can pave way for the fabrication of high-performance devices with the availability of the integration of emerging functions.⁸ The prevalent processing method disperses micro- and nano-sized particles of conducting polymers in plastic matrices for the fabrication of functional composites. Nevertheless, high doping levels will inevitably cause a dramatic change of the intrinsic properties of the plastics and the deterioration of their longtermed durability.

As an alternative approach, conducing polymer-based films render plastics to possess interesting optical, chemical, and electrical properties, and in the meantime, can maintain the bulk properties of the plastics.9 It nonetheless remains technically challenging to design general approaches to deposit uniform conducting polymer thin films on plastic substrates ascribed to the poor processability of conducting polymers. Traditional, solution-processed deposition of conducting polymers on plastic substrates often led to thick coatings usually hundreds of nanometers in thickness or beyond, and poor adhesion is inevitable owing to the stiffness of conducting polymer chains and their limited van der Waals interactions with the substrate.^{10,11} The solution-based method only made success in delivering poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) thin films on plastic substrates owing to the good solubility of PEDOT in water and organic solvents in the presence of PSS dopants.^{12,13} The increased hydrophilicity in the resulting PEDOT:PSS coatings nevertheless brings in long-term stability issues owing to the dissociation of the PSS constituents. In recent years, the Gleason group proposed an emerging method, namely, oxidative chemical vapor deposition to synthesize conducting polymer thin films.^{14,15} This green approach is advantageous for providing precise thickness control and good adhesion of thin films on substrates, processing simplicity, and importantly,

Received: April 27, 2020 Revised: June 28, 2020 Published: July 16, 2020





Scheme 1. Schematic Illustration of the Fabrication Route to PEGylated PANI Nanocoatings on PC Containing Multiple Steps; Photos of Corresponding Plastic Sheets are Shown Underneath; Each Sheet is 1 cm in Size



the green reacting environment. However, it remains imperative to develop solution-based alternatives to deposit conducting polymer thin films on plastics. To date, controllable, solution-based approaches for the formation of polyaniline (PANI) and polypyrene (PPY) thin films on ambient plastics remain missing, although anchoring their oligomeric counterparts on individual plastics gives rise to antifouling performance to exemplary plastics.¹⁶

Previous studies have confirmed that the integration with conducting polymers can help plastics to overcome biofouling irresistance in the aqueous environment, as fouling can cause the structural or other functional deficiencies of plastics.^{2,4,6,7,17-20} For instance, polysulfone and polyvinylidene fluoride membranes blended with nanofibrillar PANI dopants have shown improved permeability and antifouling performance, ascribed to the hydrophilicity of PANI achievable via chemical modification, ionic pairing, or surfactant adsorption.²¹⁻²⁵ Nevertheless, the intrinsic, antifouling performance of conducting polymers remains moderate, and it can be adapted via the interfacial modification with hydrophilic polymer chains, which resist the adhesion of cells by minimizing the intermolecular interactions between extracellular biomolecules and synthetic surfaces so that an adhered cell is readily released under a moderate shear force.^{26–32} Prior studies have identified polyethylene glycol (PEG) as a nontoxic, antifouling candidate, as the sufficiently low interfacial energy between PEGylated surfaces and water gives rise to the release of proteins and cells.³³⁻³⁵ PEGylation therefore has become a reliable process to couple the target molecules, macromolecules, colloids, vesicles, and surfaces with antifouling properties, and found widespread applications from marine industries to biomedical applications.³⁶⁻⁴² In a previous study, nanofibrous PEGylated PANI with electric conductivity and excellent antifouling performance was used as sensitive and selective electrodes, which might have great potential in biomedical applications.⁴² Therefore, the establishment of uniform thin films based on PEGylated conducting polymers can become an efficient approach for the integration of antifouling performance and emergent functions on plastic substrates without changing their intrinsic properties. Design of a general, solution-based route to couple uniform PEGylated conducting polymer thin films to ambient plastic substrates remains missing. Here, we report a controllable approach for the solution-based deposition of uniform PANI and PEGylated PANI nanocoatings on three exemplary plastic substrates. The multistep procedure (Scheme 1) started with the formation of uniform, lyotropic $V_2O_5 \cdot nH_2O$ thin films on planar plastics via spin-coating by using aqueous dispersions comprising both V₂O₅·nH₂O nanofibers and the surfactant-sodium Nlauroylsarcosinate. In situ, oxidative polymerization next transformed the $V_2O_5 \cdot nH_2O$ nanofibers to nanofibrous PANI, where individual V_2O_5 $\cdot nH_2O$ nanofibers functioned as both oxidant agents and sacrificing templates. PEGylated PANI

nanocoatings were consequently obtained by interfacial functionalization, where the presence of hydrophilic moieties on nanofibrous PANI structures was confirmed using both spectroscopy and microscopy tools. The antifouling performance of both PANI and PEGylated PANI nanocoatings was finally evaluated against bovine serum albumin (BSA) and a marine fouling bacterium *Pseudoalteromonas* sp. The approach disclosed herein delivered PEGylated PANI nanocoatings of variable thickness on multiple plastic substrates successfully, and therefore, could show great potential in antifouling applications in marine and biomedical fields.

EXPERIMENTAL SECTION

Materials. Polycarbonate (PC), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) sheets were purchased from Jinqiao Plastic Company. Both ammonium metavanadate (NH₄VO₃) powders and hydrochloric acid (HCl; 12 M) solutions were purchased from the Xilong Chemical. Aniline monomer and phosphate buffer saline solution (0.2 M; pH = 7.4) were purchased from Hushi Chemical. 4arm-PEG-COOH (average $M_{\rm p}$ = 5000 g mol⁻¹) was purchased from Jinpan Biotech Company. Pyrrole, sodium N-lauroylsarcosinate, 1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide (EDC), and N-hydroxysuccinimde (NHS) were purchased from Aladdin Industrial Corporation. BSA was purchased from Solarbio Science & Technology Co., Ltd. The bacterium Pseudoalteromonas sp. was isolated from a natural marine biofilm on the epoxy panel submerged for 7 d at a depth of 30 cm in seawater near Dalipuyu Islet (24°56'N, 118°16'E) in Xiamen Bay, China in May, 2015, and identified by the 16S rRNA gene sequence analysis. The bacterium was stored in 20% glycerol (v/v) at -80 °C. All chemicals were used as received.

Preparation of V₂O₅·nH₂O Dispersions. The synthesis of V₂O₅. nH₂O nanowire dispersion was reported in a previous study.⁴³ Accordingly, 1.0 g of NH₄VO₃ was grinded into powder with few drops of deionized (DI) water, then mixed with 10 mL of HCl (1 M) under continuous stirring. When the color of the suspension changed to red, an appropriate amount of DI water was added to obtain 20 mL suspension. After the sedimentation of red precipitate, the supernatant was removed and the red precipitate was redispersed into 20 mL of hot water (80 °C) with vigorous stirring. This process was repeated at least for three times until the red precipitate could be well-dispersed in water. Finally, the red dispersion was redispersed into 40 mL of hot water to obtain V₂O₅·nH₂O dispersions.

Preparation of PANI and Polypyrrole Nanocoatings. Plastic substrates were first ultrasonically cleaned in alternate baths of acetone, ethanol, and DI water, and dried for use. The mixture comprising 1.5 wt % $V_2O_5 \cdot nH_2O$ and 0.1 wt % sodium *N*-lauroylsarcosinate was denoted as solution A. Solution B was prepared by mixing 0.4 mL of aniline with 39.6 mL of HCl (0.1 M). Solution A was spin-coated on plastic substrates to form a uniform $V_2O_5 \cdot nH_2O$ nanocoating, then the coating substrate was soaked into solution B for 12 h to react adequately for the formation of the PANI nanocoating. The obtained PANI nanocoating was washed with 1 M HCl and DI water in sequence to remove residual $V_2O_5 \cdot nH_2O$ components. Regarding the fabrication of polypyrrole nanocoatings, solution B was prepared by mixing 0.4 mL of pyrrole with 39.6 mL of HCl (0.1 M).

pubs.acs.org/Langmuir



Figure 1. (a) Photo of a dispersion comprising $V_2O_5 \cdot nH_2O$ nanofibers, which was used for the fabrication of $V_2O_5 \cdot nH_2O$ thin films on different plastics, where each sheet is 1 cm in size. (b) TEM image of $V_2O_5 \cdot nH_2O$ nanofibers. (c) AFM image (height mode) of $V_2O_5 \cdot nH_2O$ nanofibers, where their height value is illustrated. (d,e) POM (d) and SEM (e) images of $V_2O_5 \cdot nH_2O$ thin films. (f) AFM image (height mode) of $V_2O_5 \cdot nH_2O$ thin films on a PC substrate with its thickness being measured.

Preparation of PEGylated PANI Nanocoatings. To graft 4arm-PEG-COOH onto the surface of the PANI nanocoating, the PANI nanocoating was immersed into phosphate-buffered saline (PBS) solution (0.2 M, pH 7.4) containing 0.4 M EDC, 0.1 M NHS, and 2.0 g L⁻¹ 4arm-PEG-COOH for 2 h. The incubation of the PANI nanocoating in the 4arm-PEG-COOH solution resulted in the formation of covalent bonds between amino groups of PANI and carboxyl end groups of the PEG chains. As a result, PEGylated PANI nanocoatings on a plastic substrate were obtained.

Thickness Tests. The average thickness of PANI nanocoatings on PC-coated silicon wafers was tested with a confocal laser scanning microscope. A thin PC film was spin-coated on a polished silicon wafer before the fabrication of $V_2O_5 \cdot nH_2O$ thin films. Next, $V_2O_5 \cdot nH_2O$ thin films fabricated by using different spin rates (1000, 2000, 3000, and 4000 rpm for 55 s) were used for the formation of PANI nanocoatings. Scratches were created for the height measurements on a confocal laser scanning microscope.

Electric Conductivity Tests. The electrical conductivity of PANI (107 nm in thickness) and PEGylated PANI nanocoatings was determined by current–voltage measurements using the two-probe method. At least five parallel tests were performed for the measurements of each sample. All experiments were performed at room temperature (298 K). The Mastech MAS830L digital multimeter was used for the measurements.

BSA Adhesion Tests. The antibiofouling properties of the PANI and PEGylated PANI nanocoatings were investigated by adhesion experiments using BSA as a model protein. BSA was stained with fluorescein isothiocyanate (FITC) beforehand. The FITC-labeled BSA was dissolved in PBS solution (0.2 M, pH = 7.4) at a concentration of 100 μ g mL⁻¹. Pristine PC, PANI nanocoatings, and PEGylate PANI nanocoatings (1 cm in size) were first immersed in PBS solution (0.2 M, pH = 7.4) for 2 h to avoid the potential effects due to the proton impurity of PANI. Then, all of these samples were immersed in the BSA solution and incubated at 37 °C for 24 h. Afterward, the samples were rinsed with DI water and the adhesion of BSA on the three types of substrates were observed using a fluorescent microscope.

Bacterial Attachment Test. The antiattachment of the PANI and PEGylated PANI nanocoatings toward the bacterium *Pseudoalteromonas* sp. was evaluated in this work. *Pseudoalteromonas* sp. was grown overnight in 100 mL of 2216E broth on a rotary shaker (180 rpm) at 28 °C. After being centrifuged at 8000 rpm at 4 °C for 20 min, the broth supernatant was removed and the cells were suspended in sterile filtered ($0.22 \ \mu m$) seawater (FSW) to reach an optical density of 1 at 600 nm. In the bacterial attachment assay, the 6-well plates were used. A volume of 9.9 mL of FSW and 0.1 mL of bacterial suspension were added into each well, which contained a plastic

substrate $(20 \times 20 \text{ mm})$ with a PANI or PEGylate PANI nanocoating. The control well contained 9.9 mL of FSW, 0.1 mL of bacterial suspension, and a pristine plastic substrate. There were three replicates for each treatment and control. The 6-well plates were incubated for 3 h at 25 °C. Unsettled bacteria were removed from the substrates by washing gently with sterile FSW. Then, the plastic substrates were observed under a BX53 polarizing microscope. The number of adhered bacteria on each plastic substrates was counted in nine random fields of view from pictures taken with a camera (Leica DFC 420C). The density of attached bacteria was calculated as C/S, where C and S are the average number of attached bacteria and the area of an image, respectively.

Characterization. Polarized optical microscopy and optical microscopy images were obtained using an Olympus BX53 polarizing microscope equipped with a charge-coupled device (CCD) camera. Atomic force microscopy (AFM) (DI Multimode, Veeco, Inc., tapping mode) and scanning electron microscopy (ZEISS Sigma HD) were used to obtain topographical information on the thin films. TEM specimens were scraped off from the uniaxial thin films, dispersed in pure ethanol by sonication, and transferred onto carbon films. Those thin films were examined by an FEI Talos F200 environmental transmission electron microscope (Thermal Fisher Scientific). Raman spectra were recorded with a MicroRaman System RM3000 spectrometer and an argon-ion laser operating at a wavelength of 633 nm as the excitation. The attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectroscopic measurements were carried out using a Nicolet IS10 Fourier transform spectrometer (Thermo-Fisher, US) in the ATR mode with a diamond ATR attachment. UV-visible transmission spectra were recorded using an LAMBDA 750 ultraviolet spectrophotometer (PerkinElmer, USA), where pristine PC sheets were used as the reference. Confocal laser scanning microscope (VK-X200, Keyence, Japan) was used to measure the thickness of the PANI nanocoatings. The conventional contact angles were measured using a highly sensitive microelectromechanical balance system (Data-Physics DCAT11, Germany). The fluorescent optical microscopic images were taken with a Leica DFC7000T with a CCD camera. The analyses of images were performed with software ImageJ. The surface coverage values were quantified by dividing the number of colored pixels by the total number of pixels.

RESULTS AND DISCUSSION

 $V_2O_5 \cdot nH_2O$ Thin Films. The success of the multistep strategy is dependent on the formation of uniform $V_2O_5 \cdot nH_2O$ thin films on planar plastic substrates. Aqueous dispersions were composed of ribbon-like $V_2O_5 \cdot nH_2O$ nanofibers with



Figure 2. (a,b) POM (a) and SEM (b) images of PANI nanocoatings. (c) Raman spectra showing a pristine PC substrate, a $V_2O_5 \cdot nH_2O$ thin film, and a PANI nanocoating. (d) CLSM image of a scratched PANI nanocoating for the thickness measurement. (e) Curve showing spin rates vs the thickness and transparency of the PANI nanocoatings. (f) UV-vis spectra of PANI nanocoatings of varied thickness. PANI nanocoatings were deposited on PC substrates.

varied aspect ratios, depending on the ripening periods (Figure 1a,b).^{43,44} In the current study, the dispersions for spin-coating were composed of nanofibers with their length and height at $2.0 \pm 1.1 \ \mu \text{m}$ and $6.8 \pm 3.2 \ \text{nm} (N = 60)$, respectively (Figure 1c). The resulting aspect ratio of the nanofibers is about 312 (Figure 1c), and the extreme value tremendously increases the chance of interactions between adjacent V2O5·nH2O nanofibers. Moreover, because of the dissociation of hydroxy groups at the edge planes of the ribbon-shaped architecture,⁴ individual $V_2O_5 \cdot nH_2O$ nanofibers in the aqueous phase are weakly, negatively charged, as confirmed by the moderate zeta potential value of -5.3 mV. Lyotropic nematic phase starts to form when the concentration of $V_2O_5 \cdot nH_2O$ dispersions exceeds about 0.7 wt %, according to a previous study.44 Therefore, the interactions between $V_2O_5 \cdot nH_2O$ nanofibers are so strong that adjacent nanofibers tend to be mutually oriented in each nematic polydomain in a spontaneous manner. The ordering can be preserved or enhanced permanently in continuous $V_2O_5 \cdot nH_2O$ films⁴⁵ and thin films^{46,47} after solvent removal. In short, both extreme aspect ratios and rich interfacial hydroxy groups guarantee strong interparticulate interactions between $V_2O_5 \cdot nH_2O$ nanofibers.

Nevertheless, pristine dispersions led to discontinuous V_2O_5 . nH_2O thin films on plastic substrates (Supporting Information Figure 1a), as these hydrophobic surfaces exhibited high interfacial energy with water. The high interfacial energy between water and the plastic substrate was evaluated by using contact angle measurements. For instance, the contact angle of pristine V_2O_5 . nH_2O dispersion on a planar PC substrate was at a value of $87.9^\circ \pm 1.6^\circ$ (N = 6) (ESI Supporting Information

Figure 1b). In this circumstance, the adhered $V_2O_5 \cdot nH_2O$ nanofibers were readily detached from the plastic substrates back to the dispersion phase. The addition of sodium Nlauroylsarcosinate in V2O5:nH2O dispersions decreased the interfacial energy highly, as the contact angle of $V_2O_5 \cdot nH_2O$ dispersions in the presence of the surfactant was tremendously decreased to a value of $21.3 \pm 0.5^{\circ}$ (N = 6) (ESI Supporting Information Figure 1c). In a standard procedure, spin-coating of dispersions comprising 1.5 and 0.1 wt % V2O5 nH2O nanofibers and sodium N-lauroylsarcosinate, respectively, led to uniform thin films on plastic substrates such as PVC, PET, and PC (Figure 1d). A polarized optical microscopy (POM) image confirms the formation of continuous, lyotropic nematic thin films on PC (Figure 1e). Microscopically, an AFM image reveals that the thickness of a $V_2O_5 \cdot nH_2O$ nanofibrous thin film is about 80 nm, which is equivalent to around 10-12 layers of V_2O_5 nH₂O nanofibers in total (Figure 1f). It is worth noting that the thickness of the thin films is tunable by changing both spin-coating parameters and dispersion conditions. Multiple microscopic tools confirm the formation of continuous V2O5·nH2O thin films on plastic substrates assisted by the presence of a surfactant-sodium Nlauroylsarcosinate. To summarize, the formation of uniform V2O5·nH2O thin films on plastic substrates can be disclosed from three aspects, namely, the intrinsic properties of individual V2O5 nH2O nanofibers, the assembly behaviors of the nanofibers, and the interactions between dispersions and the plastic substrates.

PANI and PEGylated PANI Nanocoatings. V₂O₅·*n*H₂O thin films templated the formation of PANI nanocoatings,



Figure 3. (a) ATR–IR spectra of PEGylated PANI nanocoatings, where the interfacial modification of 4arm-PEG-COOH on nanofibrous PANI is shown in an inserted image. (b–d) POM (b), SEM (c), and AFM (d, height mode) images showing structural information of PEGylated PANI nanocoatings. (e) Contact angles of water on pristine PC substrates, PANI nanocoatings, and PEGylated PANI nanocoatings, and six parallel measurements were performed for the statistics.

where individual V2O5.nH2O nanofibers functioned as both sacrificing templates and oxidant agents for the in situ formation of PANI nanofibers.48 PANI nanocoatings show a uniform birefringent contrast under crossed polarizers (Figure 2a), verifying the formation of continuous nanocoatings. Moreover, an exemplary SEM image of the same coating confirms that it is composed of densely packed nanofibers, which are reminiscent of their $V_2O_5 \cdot nH_2O$ counterparts in the nanostructural form (Figure 2b). The moderate birefringent contrast in Figure 2a discloses the relatively weak interparticulate interactions, namely, hydrophobic interactions, between adjacent PANI nanofibers, which is in sharp contrast with relatively strong hydrogen bonding interactions in the corresponding $V_2O_5 \cdot nH_2O$ counterparts (Figure 1e). It is worth noting that the collective behaviors of hydrophobic forces between adjacent nanofibrous PANI guarantee not only the uniformity of PANI nanocoatings, but give rise to good adhesion with plastic substrates of hydrophobic nature.

Next, the formation of PANI nanocoatings was confirmed with Raman spectroscopy. The characteristic Raman peaks at 1588 and 1484 cm⁻¹ (Figure 2c) are assigned to the stretching of C=C and C=N groups of the quinoid units of PANI, respectively. Moreover, the peak at 1215 cm⁻¹ belongs to the

deformation of the inplane ring of quinoid units, and that at 1159 cm⁻¹ is attributed to C-H bending of phenyl units of PANI. Additionally, out-of-plane deformations of the ring are attributed to the bands at 520 and 423 cm⁻¹, respectively, and the broad structural band at 778 cm⁻¹ reflects benzene-ring deformations of variously substituted aromatic rings. No Raman peak belonging to the V2O5 nH2O constituents was detected, which confirmed the chemical purity of the PANI nanocoating. Moreover, energy dispersive X-ray was conducted to verify the absence of vanadium element in the PANI nanocoating (ESI Supporting Information Figure 2). The oxidative polymerization of aniline by using $V_2O_5 \cdot nH_2O$ dispersions as oxidant agents was first reported by Kanatzidis and co-workers.⁴⁸ Although the detailed mechanism of *in situ*, oxidative polymerization remained in debate,⁴⁹ our previous studies have verified that individual V2O5.nH2O nanofibers functioned as sacrificing templates for the formation of nanofibrous PANI.^{46,50} Based on the hydrophobic interparticulate interactions between nanofibrillar PANI, multiple structural forms such as thin films,⁴⁶ fibers,⁵¹ and 3D networks^{50,52} could be permanently maintained after oxidative polymerization using $V_2O_5 \cdot nH_2O$ dispersions or (thin) films as oxidant agents. It is worth noting that the method based on in



Figure 4. (a) Schematic of PEGylated PANI nanocoatings showing antifouling performance. (b) Coverage percentages of BSA on three pristine plastic substrates, PANI nanocoatings, and PEGylated PANI nanocoatings after an adsorption period of 48 h. (c) Fluorescent microscopy images of BSA adsorption on pristine PC, a PANI nanocoating, and a PEGylated PANI nanocoating. The adsorption period is 48 h. Scale bar: 500 μ m. (d) Cell density of *Pseudoalteromonas* sp. attached on pristine plastic substrates, PANI nanocoatings on the three substrates, and PEGylated PANI nanocoatings on the three substrates. In figures b and d, data with significant difference among treatments (p < 0.05) according to a Turkey test are indicated by different letters above the bars.

situ, oxidative polymerization was equally valid for the fabrication of other conducting polymers including polypyrrole^{50,53} and poly(3,4-ethylenedioxythiophene).^{47,54} For instance, Ouyang and co-workers fabricated uniform PEDOT nanocoatings on hydrophilic substrates.⁴⁷ Here, pure PANI nanocoatings have been deposited on hydrophobic plastic substrates successfully in the presence of sodium *N*-lauroylsarcosinate. The current method was readily extended for the fabrication of PPY nanocoatings on PC substrates (ESI Supporting Information Figure 3a–c). Therefore, the strategy introduced herein can be a general strategy for the fabrication of conducting polymer nanocoatings on plastic substrates.

The thickness and light transmittance of PANI nanocoatings can be indirectly controlled by tuning spin rates of $V_2O_5 \cdot nH_2O_5$ dispersions. The thickness of PANI nanocoatings decreased with the increase of spin rates, as confirmed by using confocal laser scanning microscopy (CLSM) technique (Figure 2d). When the spin rates of $V_2O_5 \cdot nH_2O$ dispersions was increased from 1000 to 4000 rpm, the thickness of the corresponding PANI nanocoatings was decreased from 107.0 \pm 17.5 to 19.0 \pm 4.0 nm (ESI Supporting Information Figure 4a-c). The CLSM images depict that the nanocoatings are uniform in height statistics. Moreover, the increased thickness of the PANI nanocoatings caused the decrease in light transparency (Figure 2e). For instance, the transmittance of PANI nanocoatings in the visible region (between 400 and 800 nm) with a thickness of ~90 nm and ~20 nm was approximately ~80 and ~90%, respectively, evaluated with

diffuse reflectance ultraviolet-visible spectrophotometry (Figure 2f). Light transparency of \sim 90% of nanocoatings is close to that of ITO glass, and therefore can be approached for transparent applications.

The success of the solution-based method of fabrication of conducting polymer nanocoatings on plastics lies in the use of lyotropic colloidal oxidant, namely, V2O5:nH2O nanofibers, which, in a spin-coating process, can form continuous thin films in the presence of surfactants. Although it has long been known that specific oxidants, exemplified by Fe(III) tosylate, can form continuous thin coatings via solution-casting or spincoating, the treatment can only proceed on hydrophilic substrates.⁵⁵ To our knowledge, oxidative chemical vapor deposition, to date, is the only reliable method to deposit uniform conducting polymer nanocoatings on plastic substrates.⁵⁶ The method proceeding in a closed chamber is characteristic of being a dynamic process, which requires heated power to vaporize oxidant agents to generate sufficient oxidant flux and precise control of reaction parameters such as substrate temperature and monomer vapor pressure to achieve uniform nanocoatings with preferred conjugation length, configuration, and high electric conductivity.^{14,15} As a comparison, the uniform $V_2O_5 \cdot nH_2O$ thin film formed in our approach herein turned the subsequent oxidation polymerization to an easy process, and the polymerization degree was complete, as no $V_2O_5 \cdot nH_2O$ constitute was detectable in the resulting PANI nanocoatings. It is worth noting that the *in situ*, oxidative polymerization, in principle, can also proceed in the

vapor phase. It is also anticipated that beyond V_2O_5 · nH_2O nanofibers, other shape-anisotropic colloids of metal oxides can also form uniform thin films on substrates of different wetting behaviors and function as a coupled sacrificing template and oxidant agent for the formation of conducting polymer nanocoatings.

Next, PEGylated PANI nanocoatings were prepared to improve the hydration level, which was deemed as a key parameter determining the antifouling performance. PEG was grafted on the surface of nanofibrous PANI through the covalent interaction between the amino groups exposed on the end of the PANI segment and the carboxyl groups on 4arm-PEG-COOH, leading to the formation of PEGylated PANI nanocoatings.⁴² The formation of PEGylated PANI nanocoatings was confirmed by FTIR spectroscopy (Figure 3a), where the peak appeared at 1644 and 1245 cm⁻¹ were ascribed to amine bands on the PEG chain.⁴² Additionally, peaks that appeared at 1051, 2873, and 2969 cm^{-1} were ascribed to C–O symmetric stretching, -CH₃ symmetric stretching, and -CH₃ asymmetric stretching, respectively. The FTIR spectra clearly revealed that PEG chains were covalently attached onto nanofibrous PANI through the formation of amide bonds.^{40,42} PEGylated PANI nanocoatings show a strong birefringent contrast, which is different from their pristine PANI counterparts (Figure 3b). The reappearance of the birefringent contrast suggests the presence of strong interparticulate interactions between PEGylated PANI nanofibers, which can be ascribed to steric repulsions between adjacent PEG chains. The presence of the PEG layer can be visualized using microscopy techniques. Both SEM and AFM images show the presence of necklace-like nanodomains on nanofibrous PANI (Figure 3c,d), which can be convincingly attributed to the presence of PEG chains. As a comparison, pristine nanofibrous PANI are smooth on the surface (ESI Supporting Information Figure 5). It is hypothesized that the necklace-shaped nanodomains homogeneously distributed on nanofibrous PANI were formed ascribed to the shrinkage of PEG brushes after solvent removal. PEGylated PANI nanocoatings show the enhanced hydrophilicity in comparison with their pristine counterpart, as the contact angles of water on a PEGylated PANI nanocoating, a pristine PANI nanocoating, and a pristine PC are 43.6 ± 2.4 , 52.6 ± 3.8 , and $84.8 \pm 4.4^{\circ}$ (N = 6), respectively (Figure 3e). Additionally, PEGylation caused the significant decrease of electric conductivity, as PEG exhibits very low conductivity. As a comparison, its pristine PANI counterparts (107 nm in thickness) showed electric conductivity of 1.20 \pm 0.17 S cm⁻¹ (N = 3).

Evaluation of Antifouling Performance. In the current work, a protein (BSA) and a bacterium (Pseudoalteromonas sp.) were used to evaluate the antifouling performances of PANI and PEGylated PANI nanocoatings (Figure 4a-d). First, three types of engineering plastics with and without nanocoatings were exposed to the BSA feed solution (0.1 g L^{-1}) in PBS. It is worth noting that BSA is a well-accepted test protein for the evaluation of antifouling performance of coating materials.⁵⁷ Quantification of the surface adsorption of BSA was conducted via fluorescence microscopy after an exposure period of 48 h. Fluorescent microscopy images reveal that for the same type of engineering plastics, the adsorption of BSA on PANI and PEGylated PANI nanocoatings was significantly decreased in comparison with that on their pristine counterpart (Figure 4c). The calculation of the number of pixels in the microscopy images of the PC series show that the adhesion

areas on pristine PC, PANI nanocoatings, and PEGylated PANI nanocoatings are 21.032 ± 7.884 , 0.347 ± 0.039 , and $0.165 \pm 0.035\%$ (N = 12), respectively (Figure 4b). In case the BSA adhesion area of pristine PC was set as the standard, the rejection rates of BSA on PANI nanocoatings and PEGylated PANI nanocoatings were 98.4 and 99.2%, respectively. The same trend was valid in PET and PVC series (Figure 4b,c and ESI Supporting Information Figure 6). It has been demonstrated that PANI exhibited modest inherent antifouling properties probably owing to its relative hydrophilicity in comparison with the inherent hydrophobicity of engineering plastics.^{21,24} Moreover, the PEGylation provides further rise on the fouling resistance of the PANI-based nanocoatings, as the highly hydrated PEG chains with conformational flexibility provide a steric barrier for the approach of BSA molecules.^{33,35}

Additionally, the advantage of the current approach lies in its capability of providing a general approach for the introduction of uniform PEGylated PANI nanocoatings on different engineering plastics. It is therefore highly desirable to compare the antifouling performance of PEGylated PANI nanocoatings deposited on different plastic substrates. Our results show that, although pristine plastics show varied adsorption of BSA, the PANI and PEGylated PANI nanocoatings on PC, PET, and PVC, respectively, exhibit similar capability of BSA adsorption (Figure 4b). Therefore, the BSA adsorption experiments demonstrate that the method introduced herein integrated PEGylated PANI nanocoatings on multiple types of plastics, bringing in similar antifouling properties.

The good fouling resistance against BSA leads us to test the nanocoatings against the marine fouling bacterium *Pseudoalteromonas* sp. Although the bacteria showed different attachments on the three pristine plastic substrates owing to their different interfacial characteristics, PANI nanocoatings on the three plastics led to similar bacterial attachment results, which suggested that the bacterial attachment on the modified plastics was mainly dependent on the presence of the nanocoatings instead of the plastics themselves. Compared with the PANI nanocoatings, the PEGylated PANI nanocoatings showed significant decrease in the bacterial attachment (Figure 4d). Therefore, the antifouling effect of the PEGylated PANI nanocoating against marine bacteria should be ascribed to the introduction of hydrophilic layers *via* PEGylation.⁵⁸

CONCLUSIONS

The formation of $V_2O_5 \cdot nH_2O$ nanofibrous networks assisted by surfactants guarantees the integration of PANI and PEGylated PANI nanocoatings and related antifouling properties with multiple engineering plastics. The strategy based on the coupling of assembly of shape-anisotropic nanocolloids and in situ, oxidative polymerization opens an avenue for the formation of uniform, conducting polymer-based nanocoatings on multiple hydrophobic surfaces, irrelevant of their varied chemical information. Although the current study highlighted the antifouling performance of the PANI-based nanocoatings, these nanocoatings also possess interesting optical, chemical, electrical, and mechanical properties, which will have great impact in energy research, electronic device fabrication, and biomedical research. Considering the rapidly growing number of synthetic and biogenic one-dimensional nanocolloids with distinct inherent properties, geometric information, and interfacial characteristics, we are optimistic that the solutionbased coating approach can be readily extended for the

Langmuir

fabrication of a broad spectrum of one-dimensional nanocolloid-based thin films on ambient hydrophobic surfaces, combining the inherent properties of the substrate with the emergent ones generated from the nanocoatings.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c01223.

Digital photo of discontinuous $V_2O_5 \cdot nH_2O$ thin films, contact angle of $V_2O_5 \cdot nH_2O$ dispersion, energy dispersive X-ray composition analysis of PANI nanocoating, POM and scanning electron microscopy images of polypyrrole nanocoatings, AFM and confocal laser scanning microscopy images of PANI nanocoating, and fluorescence microscopy images of BSA adhesion tests on PVC and PET substrates (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Qingchi Xu Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China; Email: xuqingchi@ xmu.edu.cn
- Danqing Feng Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China; Email: dqfeng@xmu.edu.cn
- Yuan Jiang Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China; orcid.org/0000-0002-1669-8023; Email: yuan.jiang@xmu.edu.cn

Authors

- **Chen-Xi Shuai** Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China
- Yuan He Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China
- Pei Su Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China

- Qiaoling Huang Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China; orcid.org/0000-0001-9665-1542
- **Deng Pan** Department of Physics, College of Ocean & Earth Sciences, College of Materials, State-Province Joint Engineering Laboratory of Marine Bioproducts and Technology, Research Institute for Biomimetics and Soft Matter, Fujian Provincial Key Laboratory for Soft Functional Materials Research, Xiamen University, Xiamen 361005, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.langmuir.0c01223

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge financial supports from the National Natural Science Foundation of China (21303144, 21875193), the Natural Science Foundation of Fujian Province of China (2018J05025), the Fundamental Research Funds for the Central Universities (20720180016, 20720180066), and the Science and Technology Project of Fujian Province (2018Y0076). Prof. Dongtao Ge, Prof. Hua Bai, Dr. Taoran Lin, Dr. Likun Yang, Yange Wang, Xiuming Zhang, Xinyu Liu, and Shenshi Guo are acknowledged for characterization assistance. We thank An'an Zhou, Yue-e Wen, Yu-xuan Feng, and Xuyi Li for experiment assistance.

REFERENCES

(1) Forrest, S. R. The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* **2004**, *428*, 911–918.

(2) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Mariñas, B. J.; Mayes, A. M. Science and technology for water purification in the coming decades. *Nature* **2008**, *452*, 301–310.

(3) Rogers, J. A.; Someya, T.; Huang, Y. Materials and Mechanics for Stretchable Electronics. *Science* **2010**, *327*, 1603–1607.

(4) Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Müller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. Emerging applications of stimuli-responsive polymer materials. *Nat. Mater.* **2010**, *9*, 101–113.

(5) Kaltenbrunner, M.; Sekitani, T.; Reeder, J.; Yokota, T.; Kuribara, K.; Tokuhara, T.; Drack, M.; Schwödiauer, R.; Graz, I.; Bauer-Gogonea, S.; Bauer, S.; Someya, T. An ultra-lightweight design for imperceptible plastic electronics. *Nature* **2013**, *499*, 458–463.

(6) Gao, W.; Emaminejad, S.; Nyein, H. Y. Y.; Challa, S.; Chen, K.; Peck, A.; Fahad, H. M.; Ota, H.; Shiraki, H.; Kiriya, D.; Lien, D.-H.; Brooks, G. A.; Davis, R. W.; Javey, A. Fully integrated wearable sensor arrays for multiplexed in situ perspiration analysis. *Nature* **2016**, *529*, 509–514.

(7) Werber, J. R.; Osuji, C. O.; Elimelech, M. Materials for nextgeneration desalination and water purification membranes. *Nat. Rev. Mater.* **2016**, *1*, 16018.

(8) Baker, C. O.; Huang, X.; Nelson, W.; Kaner, R. B. Polyaniline nanofibers: broadening applications for conducting polymers. *Chem. Soc. Rev.* 2017, 46, 1510–1525.

(9) Someya, T.; Bao, Z.; Malliaras, G. G. The rise of plastic bioelectronics. *Nature* 2016, 540, 379–385.

(10) Wu, J.; Zhou, D.; Too, C. O.; Wallace, G. G. Conducting polymer coated lycra. *Synth. Met.* **2005**, *155*, 698–701.

(11) Yue, B.; Wang, C.; Ding, X.; Wallace, G. G. Polypyrrole coated nylon lycra fabric as stretchable electrode for supercapacitor applications. *Electrochim. Acta* **2012**, *68*, 18–24.

(12) Hokazono, M.; Anno, H.; Toshima, N. Thermoelectric Properties and Thermal Stability of PEDOT:PSS Films on a Polyimide Substrate and Application in Flexible Energy Conversion Devices. J. Electron. Mater. **2014**, 43, 2196–2201.

(13) Shi, H.; Liu, C.; Jiang, Q.; Xu, J. Effective Approaches to Improve the Electrical Conductivity of PEDOT:PSS: A Review. *Adv. Electron. Mater.* **2015**, *1*, 1500017.

(14) Lock, J. P.; Im, S. G.; Gleason, K. K. Oxidative Chemical Vapor Deposition of Electrically Conducting Poly(3,4-ethylenedioxythiophene) Films. *Macromolecules* **2006**, *39*, 5326–5329.

(15) Tenhaeff, W. E.; Gleason, K. K. Initiated and Oxidative Chemical Vapor Deposition of Polymeric Thin Films: iCVD and oCVD. *Adv. Funct. Mater.* **2008**, *18*, 979–992.

(16) Lin, C.-W.; Aguilar, S.; Rao, E.; Mak, W. H.; Huang, X.; He, N.; Chen, D.; Jun, D.; Curson, P. A.; McVerry, B. T.; Hoek, E. M. V.; Huang, S.-C.; Kaner, R. B. Direct grafting of tetraaniline via perfluorophenylazide photochemistry to create antifouling, low bioadhesion surfaces. *Chem. Sci.* **2019**, *10*, 4445–4457.

(17) Wong, I.; Ho, C.-M. Surface molecular property modifications for poly(dimethylsiloxane) (PDMS) based microfluidic devices. *Microfluid. Nanofluidics* **2009**, *7*, 291.

(18) Liu, F.; Hashim, N. A.; Liu, Y.; Abed, M. R. M.; Li, K. Progress in the production and modification of PVDF membranes. *J. Membr. Sci.* **2011**, 375, 1–27.

(19) Ren, K.; Zhou, J.; Wu, H. Materials for Microfluidic Chip Fabrication. Acc. Chem. Res. 2013, 46, 2396–2406.

(20) Hou, X.; Hu, Y.; Grinthal, A.; Khan, M.; Aizenberg, J. Liquidbased gating mechanism with tunable multiphase selectivity and antifouling behaviour. *Nature* **2015**, *519*, 70–73.

(21) Fan, Z.; Wang, Z.; Sun, N.; Wang, J.; Wang, S. Performance improvement of polysulfone ultrafiltration membrane by blending with polyaniline nanofibers. *J. Membr. Sci.* **2008**, *320*, 363–371.

(22) Zhao, S.; Wang, Z.; Wei, X.; Zhao, B.; Wang, J.; Yang, S.; Wang, S. Performance improvement of polysulfone ultrafiltration membrane using PANiEB as both pore forming agent and hydrophilic modifier. *J. Membr. Sci.* **2011**, 385–386, 251–262.

(23) Zhao, S.; Wang, Z.; Wei, X.; Zhao, B.; Wang, J.; Yang, S.; Wang, S. Performance Improvement of Polysulfone Ultrafiltration Membrane Using Well-Dispersed Polyaniline-Poly(vinylpyrrolidone) Nanocomposite as the Additive. *Ind. Eng. Chem. Res.* **2012**, *51*, 4661–4672.

(24) McVerry, B. T.; Temple, J. A. T.; Huang, X.; Marsh, K. L.; Hoek, E. M. V.; Kaner, R. B. Fabrication of Low-Fouling Ultrafiltration Membranes Using a Hydrophilic, Self-Doping Polyaniline Additive. *Chem. Mater.* **2013**, *25*, 3597–3602.

(25) Zhao, X.; He, C. Efficient Preparation of Super Antifouling PVDF Ultrafiltration Membrane with One Step Fabricated Zwitterionic Surface. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17947–17953.

(26) Jiang, S.; Cao, Z. Ultralow-Fouling, Functionalizable, and Hydrolyzable Zwitterionic Materials and Their Derivatives for Biological Applications. *Adv. Mater.* **2010**, *22*, 920–932.

(27) Banerjee, I.; Pangule, R. C.; Kane, R. S. Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms. *Adv. Mater.* **2011**, *23*, 690–718.

(28) Lejars, M.; Margaillan, A.; Bressy, C. Fouling Release Coatings: A Nontoxic Alternative to Biocidal Antifouling Coatings. *Chem. Rev.* **2012**, *112*, 4347–4390.

(29) Xiao, L.; Li, J.; Mieszkin, S.; Di Fino, A.; Clare, A. S.; Callow, M. E.; Callow, J. A.; Grunze, M.; Rosenhahn, A.; Levkin, P. A. Slippery Liquid-Infused Porous Surfaces Showing Marine Antibiofouling Properties. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10074–10080.

(30) Yang, W. J.; Neoh, K.-G.; Kang, E.-T.; Teo, S. L.-M.; Rittschof, D. Polymer brush coatings for combating marine biofouling. *Prog. Polym. Sci.* **2014**, *39*, 1017–1042.

(31) Wei, Q.; Becherer, T.; Angioletti-Uberti, S.; Dzubiella, J.; Wischke, C.; Neffe, A. T.; Lendlein, A.; Ballauff, M.; Haag, R. Protein Interactions with Polymer Coatings and Biomaterials. *Angew. Chem., Int. Ed.* **2014**, *53*, 8004–8031.

(32) Yang, R.; Jang, H.; Stocker, R.; Gleason, K. K. Synergistic Prevention of Biofouling in Seawater Desalination by Zwitterionic Surfaces and Low-Level Chlorination. *Adv. Mater.* **2014**, *26*, 1711–1718.

(33) Hucknall, A.; Rangarajan, S.; Chilkoti, A. In Pursuit of Zero: Polymer Brushes that Resist the Adsorption of Proteins. *Adv. Mater.* **2009**, *21*, 2441–2446.

(34) Calderón, M.; Quadir, M. A.; Sharma, S. K.; Haag, R. Dendritic Polyglycerols for Biomedical Applications. *Adv. Mater.* **2010**, *22*, 190–218.

(35) Rosenhahn, A.; Schilp, S.; Kreuzer, H. J.; Grunze, M. The role of "inert" surface chemistry in marine biofouling prevention. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4275–4286.

(36) Otsuka, H.; Nagasaki, Y.; Kataoka, K. Self-assembly of poly(ethylene glycol)-based block copolymers for biomedical applications. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 3–10.

(37) Wang, P.; Tan, K. L.; Kang, E. T.; Neoh, K. G. Plasma-induced immobilization of poly(ethylene glycol) onto poly(vinylidene fluoride) microporous membrane. J. Membr. Sci. 2002, 195, 103–114.

(38) Lee, S.; Vörös, J. An Aqueous-Based Surface Modification of Poly(dimethylsiloxane) with Poly(ethylene glycol) to Prevent Biofouling. *Langmuir* **2005**, *21*, 11957–11962.

(39) Sagle, A. C.; Van Wagner, E. M.; Ju, H.; McCloskey, B. D.; Freeman, B. D.; Sharma, M. M. PEG-coated reverse osmosis membranes: Desalination properties and fouling resistance. *J. Membr. Sci.* **2009**, *340*, 92–108.

(40) Kang, G.; Liu, M.; Lin, B.; Cao, Y.; Yuan, Q. A novel method of surface modification on thin-film composite reverse osmosis membrane by grafting poly(ethylene glycol). *Polymer* **2007**, *48*, 1165–1170.

(41) Fan, X.; Su, Y.; Zhao, X.; Li, Y.; Zhang, R.; Ma, T.; Liu, Y.; Jiang, Z. Manipulating the segregation behavior of polyethylene glycol by hydrogen bonding interaction to endow ultrafiltration membranes with enhanced antifouling performance. *J. Membr. Sci.* **2016**, *499*, 56–64.

(42) Hui, N.; Sun, X.; Niu, S.; Luo, X. PEGylated Polyaniline Nanofibers: Antifouling and Conducting Biomaterial for Electrochemical DNA Sensing. *ACS Appl. Mater. Interfaces* **2017**, *9*, 2914–2923.

(43) Lausser, C.; Cölfen, H.; Antonietti, M. Mesocrystals of Vanadium Pentoxide: A Comparative Evaluation of Three Different Pathways of Mesocrystal Synthesis from Tactosol Precursors. *ACS Nano* **2011**, *5*, 107–114.

(44) Livage, J. Vanadium pentoxide gels. Chem. Mater. 1991, 3, 578-593.

(45) Burghard, Z.; Leineweber, A.; van Aken, P. A.; Dufaux, T.; Burghard, M.; Bill, J. Hydrogen-Bond Reinforced Vanadia Nanofiber Paper of High Stiffness. *Adv. Mater.* **2013**, *25*, 2468–2473.

(46) Qi, X.; Lu, Z.; You, E.-M.; He, Y.; Zhang, Q.-e.; Yi, H.-J.; Li, D.; Ding, S.-Y.; Jiang, Y.; Xiong, X.; Xu, J.; Ge, D.; Liu, X. Y.; Bai, H. Nanocombing Effect Leads to Nanowire-Based, in-Plane, Uniaxial Thin Films. ACS Nano 2018, 12, 12701–12712.

(47) Chen, R.; Sun, K.; Zhang, Q.; Zhou, Y.; Li, M.; Sun, Y.; Wu, Z.; Wu, Y.; Li, X.; Xi, J.; Ma, C.; Zhang, Y.; Ouyang, J. Sequential Solution Polymerization of Poly(3,4-ethylenedioxythiophene) Using V2O5 as Oxidant for Flexible Touch Sensors. *iScience* **2019**, *12*, 66–75.

(48) Kanatzidis, M. G.; Wu, C. G.; Marcy, H. O.; Kannewurf, C. R. Conductive-polymer bronzes. Intercalated polyaniline in vanadium oxide xerogels. *J. Am. Chem. Soc.* **1989**, *111*, 4139–4141.

(49) Tran, H. D.; Li, D.; Kaner, R. B. One-Dimensional Conducting Polymer Nanostructures: Bulk Synthesis and Applications. *Adv. Mater.* **2009**, *21*, 1487–1499.

(50) Zhou, K.; He, Y.; Xu, Q.; Zhang, Q. e.; Zhou, A. a.; Lu, Z.; Yang, L.-K.; Jiang, Y.; Ge, D.; Liu, X. Y.; Bai, H. A Hydrogel of Ultrathin Pure Polyaniline Nanofibers: Oxidant-Templating Preparation and Supercapacitor Application. *ACS Nano* **2018**, *12*, 5888– 5894.

(51) Dexmer, J.; Leroy, C. M.; Binet, L.; Heresanu, V.; Launois, P.; Steunou, N.; Coulon, C.; Maquet, J.; Brun, N.; Livage, J.; Backov, R. Vanadium Oxide–PANI Nanocomposite-Based Macroscopic Fibers: 1D Alcohol Sensors Bearing Enhanced Toughness. *Chem. Mater.* **2008**, 20, 5541–5549.

(52) Zhang, X.; Goux, W. J.; Manohar, S. K. Synthesis of Polyaniline Nanofibers by "Nanofiber Seeding". *J. Am. Chem. Soc.* **2004**, *126*, 4502–4503.

(53) Zhang, X.; Manohar, S. K. Bulk synthesis of polypyrrole nanofibers by a seeding approach. J. Am. Chem. Soc. 2004, 126, 12714–12715.

(54) Zhang, X.; MacDiarmid, A. G.; Manohar, S. K. Chemical synthesis of PEDOT nanofibers. *Chem. Commun.* 2005, 5328–5330.

(55) Winther-Jensen, B.; West, K. Vapor-Phase Polymerization of 3,4-Ethylenedioxythiophene: A Route to Highly Conducting Polymer Surface Layers. *Macromolecules* **2004**, *37*, 4538–4543.

(56) Im, S. G.; Yoo, P. J.; Hammond, P. T.; Gleason, K. K. Grafted Conducting Polymer Films for Nano-patterning onto Various Organic and Inorganic Substrates by Oxidative Chemical Vapor Deposition. *Adv. Mater.* **2007**, *19*, 2863–2867.

(57) Lee, S.; Boo, C.; Elimelech, M.; Hong, S. Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO). *J. Membr. Sci.* **2010**, 365, 34–39.

(58) Nejadnik, M. R.; van der Mei, H. C.; Norde, W.; Busscher, H. J. Bacterial adhesion and growth on a polymer brush-coating. *Biomaterials* **2008**, *29*, 4117–4121.