Elucidation of Titanium Dioxide Nucleation and Growth on a Polydopamine-Modified Nanoporous Polyvinylidene Fluoride Substrate via Low-Temperature Atomic Layer Deposition

Audra DeStefano,† Jiashi Yin,† Theodore J. Kraus,‡ Bruce A. Parkinson,‡ and Katie Dongmei Li-Oakey*†

†Department of Chemical Engineering and ‡Chemistry Department, University of Wyoming, 1000 E. University Avenue, Laramie, Wyoming 82071, United States

Supporting Information

ABSTRACT: Interfaces combining polydopamine (PDA) and nanoparticles have been widely utilized for fabricating hybrid colloidal particles, thin films, and membranes for applications spanning biosensing, drug delivery, heavy metal detection, antifouling membranes, and lithium ion batteries. However, fundamental understanding of the interaction between PDA and nanoparticles is still limited, especially the impact of PDA on nanoparticle nucleation and growth. In this work, PDA is used to generate functional bonding sites for depositing titanium dioxide (TiO\textsubscript{2}) via atomic layer deposition (ALD) onto a nanoporous polymer substrate for a range of ALD cycles (<100). The resulting hybrid membranes are systematically characterized using water contact angle, scanning electron microscopy, atomic force microscopy, nitrogen adsorption and desorption, and X-ray photoelectron spectroscopy (XPS). An intriguing nonlinear relationship was observed between the number of ALD cycles and changes in surface properties (water contact angle and surface roughness). Together with XPS study, those changes in surface properties were exploited to probe the nanoparticle nucleation and growth process on complex PDA-coated porous polymer substrates. Molecular level understanding of inorganic and polymer material interfaces will shed light on fine-tuning nanoparticle-modified polymeric membrane materials.

1. INTRODUCTION

Significant effort has been invested into incorporating nanomaterials directly into polymer matrices, metal oxide frameworks, or covalent organic frameworks (COFs) for applications including mixed matrix membranes, biomedical applications, nanostructured membrane surfaces, and catalysts.1,2 However, till now theoretical predictions of composite material functions have not been met, often due to lack of fundamental understanding on atomic or molecular level interactions at the interface of metal or ceramic nanoparticles (NPs) and polymeric substrates.1,3 To fully realize the potential of materials involving NPs and polymer substrates (in either spherical or planar morphology), molecular level understanding of interfacial interactions between inorganic NPs and their substrates needs to be developed.1,4

Specifically, surface or interface property modification using covalent bonds and/or NPs has been extensively reported for applications in the fields of clean energy, membrane separation, and biomedicine to improve functionality, biocompatibility, or fouling resistance.5–9 Because of its versatile application and ease of functionalization, dopamine has been used to modify surface properties of organic polymers, metal oxides, and noble metals, after the initial report by Lee et al.9–12 Direct deposition has been used primarily to render surfaces more hydrophilic for a variety of applications, such as improving the water dispersibility of nanoporous graphene foams for membrane protein extraction.13–17 Dopamine-treated surfaces can be further functionalized using catalytic NPs, such as titanium dioxide (TiO\textsubscript{2}); self-assembly monolayer reagents, including n-dodecyl mercaptan; or securing proteins, such as aquaporins, to further optimize surface properties, including increasing antifouling resistance.1,13,18–22 Using polydopamine (PDA) as a grafting material can be particularly useful in sensing applications, including the detection of heavy metals such as lead and cadmium using PDA and Fe\textsubscript{3}O\textsubscript{4} core–shell NPs, biomolecule sensing through the immobilization of glucose oxidase for glucose sensors, and detection of small organic molecules, such as hydrogen peroxide sensors based on PDA-entrapped G-quadruplex-hemin DNAzyme.9,23–25 Despite the wide use of dopamine-assisted surface modification

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techniques, fundamental questions remain regarding how surface properties, such as roughness, contact angle, and surface chemical species, change on an atomic or molecular level, especially after the further incorporation of NPs. In addition, correlations between these properties and resultant hybrid/composite material interfaces must be carefully examined to fine-tune surface treatments for targeted applications.

Catalytic and photocatalytic NPs have been reported for various applications, including mitigating membrane fouling and developing antimicrobial surfaces. To address the particle aggregation challenge observed in liquid-phase deposition, vapor-phase deposition, especially the atomic layer deposition (ALD) technique, has been recently investigated. Thanks to its inherent self-limiting nature, ALD as a vapor-phase deposition technique allows molecular, even atomic, level control of the particle deposition process by tuning the number of ALD cycles. In addition, recent breakthroughs in spatial ALD, where reactant exposure is separated by space rather than time by moving the substrate or the spray nozzles, now enable ALD to be easily incorporated into continuous processes, reducing precursor consumption. However, fabrication of new products, such as organic light-emitting diodes, using ALD depends on improved understanding of deposition onto porous polymer substrates.

One intricacy of ALD is that adjusting the number of ALD cycles or exposure time allows gaseous reactants to penetrate into porous structures, which allows material properties to be modified on an atomic or molecular level. For example, atom clusters or NPs can be formed instead of continuous, conformal films by limiting the number of ALD cycles. This behavior is further complicated by the dependence of initial nucleation and growth on substrate properties, including surface roughness, chemistry, and porosity. Recently, subsurface nucleation was observed inside polytetrafluoroethylene and polypropylene (PP) pores because of a lack of bonding sites on the surface. To alleviate the problem, plasma pretreatment was used to generate sites for nucleation. However, surface treatment with plasma can only be applied to a limited number of materials because of its potential damage to many polymeric substrates. Alternatively, we chose PDA to generate bonding sites, which can also enhance NP adhesion via covalent bonding. Because of the wide range of materials on which PDA can be successfully bonded and its biocompatibility, this method could be extended to many sensitive materials used in applications including nanomedicine. Additionally, using a short dopamine polymerization combined with ALD treatment provides a fast, scalable approach to adjusting surface properties compared with techniques such as combined atom transfer radical polymerization and click chemistry for improving poly(vinylidene fluoride) (PVDF) cytocompatibility.

Using commercial PVDF ultrafiltration membranes as a substrate, we report how their surface properties change with a short PDA treatment time, followed by TiO₂ deposition via ALD. This system provides promise in a variety of fields because of the biocompatibility of PVDF, PDA, and TiO₂. To the best of our knowledge, PDA treatment has not been followed by ALD–TiO₂ deposition, and unlike previous reports of ALD–TiO₂ deposition directly onto PVDF, the number of ALD cycles was carefully controlled in the range of 15–90 to probe how surface properties evolve as nucleation and growth proceeds. Correlation of surface and cross-sectional properties provides an understanding on how desirable, but often competing, membrane surface properties may be best balanced for targeting specific applications.

## 2. RESULTS AND DISCUSSION

This study probes the nucleation and growth process of TiO₂ NPs on PDA-coated polymer substrates using low-temperature ALD. The inherent cyclic nature of ALD processes allows TiO₂ to be deposited molecule by molecule, providing precise control of polymer/metal oxide surface/interface properties. As discussed in the Experimental Section, PVDF ultrafiltration membranes were treated with PDA followed by ALD–TiO₂ at 100 °C using tetraakis(dimethylamido)titanium(IV) (TDMAT) and water as precursors. Although the PDA coating time was kept at 15 min, the number of ALD cycles varied from 15 to 90. Neat membranes and those treated with PDA or 15 ALD cycles were used as controls. A complete list of sample names and corresponding treatments is shown in Table 1.

### 2.1. Membrane Surface Roughness and Morphology.

Scanning electron microscopy (SEM) imaging of the top surface and cross-sectional areas was carried out for different samples. The neat, PDA, and PDA/90ALD surfaces are shown in Figure 1. Consistent structures in Figure 1a–c demonstrate

| sample ID | PDA deposition time (min) | number of ALD cycles |
|-----------|---------------------------|----------------------|
| neat      | 0                         | 0                    |
| 15ALD     | 0                         | 15                   |
| PDA       | 15                        | 0                    |
| PDA/15ALD | 15                        | 15                   |
| PDA/30ALD | 15                        | 30                   |
| PDA/60ALD | 15                        | 60                   |
| PDA/75ALD | 15                        | 75                   |
| PDA/90ALD | 15                        | 90                   |

**Figure 1.** Cross-sectional SEM images of (a) neat PVDF, (b) PDA, (c) PDA/90ALD, and (d) the top surface of PDA/90ALD. A TEM image of (e) PDA on a copper TEM grid, (f) TEM image of PDA/90ALD, and (g) TEM image of PDA/60ALD and (h) NP size distribution.
that the conditions used in ALD treatment do not significantly alter the membrane structure. Cross-sectional images were acquired for the area between the top surface and the backing material. It is worth noting that no NPs are observed on the surface or within the cross-sectional SEM images of the PDA/90ALD sample (Figure 1d), which has the largest number of ALD cycles. This may be attributed to the small size of TiO2 NPs deposited and the limitation of our SEM equipment, indicating that titanium dioxide deposition in our study (≤90 cycles of ALD) did not result in large aggregates as often observed with wet-chemistry techniques. Other groups have published SEM images of PDA on polymer substrates with deposition times longer than 15 min and have observed little changes in morphology. On the basis of the work by Kasemset et al., we expect the PDA layer to be around 1−2 nm for the deposition parameters used in this paper. Additionally, we expect an average growth rate of 0.46 Å per cycle for the conditions we report here. This suggests that a maximum coating of 6 nm (2 nm of PDA and 4 nm for 90 ALD cycles) may be possible, the nucleation and growth phase of ALD−TiO2 in this study, combined with the nanoporous polymer substrate, suggests that the amount of TiO2 deposited may be less than 4 nm.

Transmission electron microscopy (TEM) images of PDA/ALD−TiO2 depositions directly onto TEM grids provide evidence of NP growth instead of thin-film growth. The TEM image of PDA alone is shown in Figure 1e, and Figure 1f presents the TEM image of PDA/90ALD. Both images contain large dark areas attributed to PDA, but smaller (less than 6 nm) dark areas attributed to TiO2 NPs are only observed for PDA/90ALD. NP size and radial distributions were obtained through further image analysis. Size distributions for PDA/15ALD, PDA/60ALD, and PDA/90ALD samples are shown in Figure 1h. The PDA/15ALD samples show the highest fraction of small NPs. The treatment combination has fewer ALD−TiO2 cycles than the other samples considered, so the NPs are expected to be smaller. Interestingly, the PDA/60ALD sample shows a higher proportion of large NPs than the PDA/90ALD sample. This could be due to aggregation of nuclei on flexible PDA ligands and subsequent nucleation on exposed active sites. Figure 1g demonstrates that the NP spatial distribution appears to be less even for the PDA/60ALD sample than for the PDA/15ALD and 15PDA/90ALD samples.

To further understand how surface pore structures may be modified, noncontact atomic force microscopy (AFM) was used to characterize membrane surfaces (Figure 2). The key surface pore morphology appears to be modified, but the pores are not completely blocked by direct ALD−TiO2 or PDA/ALD−TiO2. Root-mean-square (rms) surface roughness measurements are plotted in Figure 2b for 5 μm × 5 μm areas. There is no significant roughness change among the samples.

Changes in pore structure and surface area were also quantified using nitrogen adsorption and desorption experiments. Resulting data were combined with Barrett, Joyner, and Halenda (BJH) theory and Brunauer, Emmett, and Teller (BET) theory to calculate the BJH average pore width (Figure 3a), BJH average pore size distribution (Figure 3b), and BET surface area (Figure 3c), respectively. Adsorption and desorption isotherms are shown in Figure S1. The shape of the isotherms is similar for different treatment combinations, but the quantity adsorbed at high relative pressure varies. 15ALD, PDA, PDA/15ALD, and PDA/60ALD adsorbed the
largest quantities of nitrogen at high relative pressure and had the largest average BET surface areas. The average pore width decreased with PDA treatment and then increased with ALD deposition from 15 to 75 cycles (Figure 3a). The consistent pore diameter between the PDA and PDA/15ALD samples shows that the ALD reactor conditions did not impact the membrane pore size and that a very small quantity of TiO₂ was deposited with only 15 ALD cycles. Further increasing ALD cycles resulted in a slight increase in the average pore width. This could be due to the blocking of pores that are smaller than 2 nm. Therefore, for all samples, the majority of pore volume is a result of small pores (Figure 3b), with 15ALD, PDA, PDA/15ALD, and PDA/60ALD samples containing the greatest total pore volume.

The BET surface area trends differ from those observed for pore size. Initially, surface area increases with PDA treatment, most likely resulting from the added pore volume by the porous PDA layer. However, TiO₂ deposition with 15 and 30 ALD cycles (PDA/15ALD and PDA/30ALD) results in a decreased surface area relative to the PDA sample, indicating that smaller pores are blocked by TiO₂ particles as they nucleate and grow. When the number of ALD cycles increases to 60, the surface area of PDA/60ALD increased, possibly due to more exposed PDA areas when TiO₂ NPs aggregated to form bigger particles, as depicted in Figure 3c. Increasing amounts of bulky, incompletely reacted TDMAT ligands on the membrane surface may also contribute to the surface area increase when ALD cycles increase from 30 to 60. Surface area decreased again when ALD cycles increased from 60 to 75 and 90, which may be attributed to pore blocking from agglomerated TiO₂ particles and additional TiO₂ nucleation and growth sites.

To summarize, the SEM, AFM, and BET results suggest that PDA and TiO₂ deposition via ALD can be used to carefully alter surface chemistry for targeted applications. Additional surface characterization results using X-ray photoelectron spectroscopy (XPS) (Figures 4 and 5) provide further insight on how surface chemistry and architecture evolve as the nucleation and growth process proceeds.

**Figure 4.** (a) Ti/F ratios for the PDA/60ALD, PDA/75ALD, and PDA/90ALD samples and (b) high-resolution Ti 2p scans for the 15ALD, PDA/15ALD, PDA/30ALD, PDA/60ALD, PDA/75ALD, and PDA/90ALD samples.

**2.2. Characterization of NP Nucleation and Growth via XPS.** XPS survey scans are shown for each ALD−TiO₂ sample, along with neat PVDF, PDA-coated PVDF, PDA-coated PVDF with ultraviolet (UV) light exposure, and 15ALD as controls in Figure S2. Additional F 1s and O 1s high-resolution scans are included in Figures S3 and S4, respectively. We note that noticeable variations in membrane surface chemistry were observed when duplicates of the neat PVDF and PDA/90ALD samples were analyzed. This is likely due to the porous and anisotropic nature of the substrates.
ally, Lee and Hon et al. used 1000 ALD cycles to deposit TiO2 because TiO2 NPs are adhered to tailored by the deposited NPs. Because the PDA chain length could aggregate without breaking the bonds between PDA and −O− of the high bond energy of Ti.6° Nonlinear changes in the Ti/F ratio with ALD cycles because of NP di-

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Figure 4b. An increase in the amount of titanium, to increase from 75 to 90. In contrast, the intensity of the Ti 2p peak linearly increased with cycle number in the range of 60−90 (Figure 4b). An increase in the amount of titanium, combined with the nonlinear Ti/F ratio progression, suggests that the fluorinated PVDF substrate initially becomes more covered with titanium (from PDA/60ALD to PDA/75ALD). However, the decreased Ti/F ratio from PDA/75ALD to PDA/90ALD suggests that more PVDF membrane surface areas were exposed after 90 cycles of ALD, while the amount of Ti increased. Considering the smaller pores (Figure 3b), smoother surfaces (Figure 3c), and comparable BET area, when ALD cycles increased from 75 to 90, we attributed the decreased Ti/F ratio with increased titanium quantity to TiO2 NP agglomeration and additional nucleation sites when further increasing ALD cycles, consistent with what was reported by Grillo et al.57 Briefly, in their study, platinum NPs grew nonlinearly onto graphene nanoplates after long exposure times (4 min) because of NP diffusion and coalescence at low temperatures (T < 100 °C). Ostwald ripening is another pathway for nonlinear growth but is unlikely to occur at low temperatures because of the high bond energies.58 Additionally, Lee and Hon et al. used 1000 ALD cycles to deposit TiO2 onto silicon and observed no Ostwald ripening below 250 °C.55 In our study, ALD experiments were carried out at 100 °C, so Ostwald ripening is unlikely to be the cause of the nonlinear changes in the Ti/F ratio with ALD cycles because of the high bond energy of Ti–O bonds.59 Alternatively, because TiO2 NPs are adhered to flexible PDA chains, NPs could aggregate without breaking the bonds between PDA and the deposited NPs. Because the PDA chain length can be tailored by fine-tuning dopamine polymerization time in air, this phenomenon may be utilized as a secondary control over deposited NP sizes in the submicron regime. Ongoing work in our group is further validating this hypothesis by direct imaging techniques, such as TEM.60

A second source of the nonlinear Ti/F ratio progression may be unreacted TDMAT precursor ligands. High-resolution N 1s XPS scans (Figure 5) were used to differentiate unreacted precursor ligands from PDA. The scans show insignificant amounts of nitrogen on the neat and 15ALD samples, but PDA deposition onto neat PVDF results in the formation of a peak at about 400 eV. The intensity of this peak grows with further incorporation of 15 ALD cycles (PDA/15ALD); however, after 30 ALD cycles, the peak begins to divide into two visible peaks. The PDA/90ALD spectrum has a shape and position similar to that of the PDA/30ALD sample but a larger area. Increasing the number of ALD cycles generally increased the N 1s peak area, with the exception from 75 to 90 ALD cycles, indicating that additional nitrogen is either incorporated into the membrane or exposed during the TiO2 deposition process. Figure 5b plots the relative N 1s component peak areas as calculated using curve fitting (fitting shown in Figures S8–S13). All samples were fitted with two peaks, with the lower energy component corresponding to C−N-type bonds and the lower energy component attributed to C=N−C-type bonds common in PDA.5,61 PDA contains numerous R–NH−R bonds, in addition to some R=−N−R bonds (about 1.3 eV lower binding energy than R−NH−R bonds), although the saturated structure R−NH−R is often reported.5,61,62

Alternatively, residual Ti=N(CH3)2 amine ligands could be present at about 398.6 eV from the unreacted precursor.63 A low-energy amine component was not observed by peak fitting, suggesting that the unreacted precursor may not play a primary role in nonlinear surface property changes. Compared to the linear relationship observed in direct TiO2 deposition onto PVDF,50 we postulate that the nonlinear observation in our study may result from the dopamine pretreatment. Decomposition or reconfiguration of PDA at elevated temperature and high-vacuum ALD conditions or X-ray-induced changes during XPS measurements could explain changes in the N 1s peak. Ongoing work in our lab is aimed at understanding the influence of temperature on PDA structure and determining the relative influences of possible NP aggregation, unreacted precursor, and changes in the PDA structure on surface chemistry and functionality.

2.3. Impact of NP Nucleation and Growth on Membrane Hydrophilicity. Another observation, as a consequence of the NP nucleation and growth mechanism of TiO2 onto PDA-pretreated PVDF, is a nonlinear water contact angle trend, as shown in Figure 6. Deposition of 15 ALD cycles of TiO2 directly onto the neat membrane resulted in an 8% decrease in water contact angle, whereas coating with 15 min of PDA lead to a larger decrease (31%). For PDA-coated

| sample  | technique  | C   | F   | N   | O   | Ti | Na | Si |
|---------|------------|-----|-----|-----|-----|----|----|----|
| PDA/15ALD | XPS       | 69.8| 16.11| 1.08| 9.48|    |    |    |
| PDA/15ALD | SEM/EDX   | 88.74|       | 6.51|    | 4.68| 0.08|
| PDA/60ALD | XPS       | 65.82| 12.3| 2.87| 15.71| 2.01|
| PDA/60ALD | SEM/EDX   | 95.54|       | 4.41| 0.06|    |    |
| PDA/90ALD | XPS       | 62.49| 18.49| 2.41| 12.97| 1.07|
| PDA/90ALD | SEM/EDX   | 90.12|       | 9.71| 0.17|    |    |

Table 2. PDA/15ALD, PDA/60ALD, and PDA/90ALD Compositions Measured by XPS and SEM/EDXS

Figure 6. (a) Water contact angles for neat, 15ALD, PDA, and PDA followed by 15/30/60/75/90 ALD cycles samples and (b) corresponding water droplet images [same sample order from left to right as panel (a)].
membranes with small amounts of ALD-deposited titanium dioxide (PDA/15ALD and PDA/30ALD), contact angles decreased linearly with increasing ALD cycles relative to the neat and PDA-coated samples. Very interestingly, the contact angle increased (from 34° to 69°) when the number of ALD cycles further increased from 30 to 60 before decreasing again with additional ALD cycles. Nikkola et al. reported a similar contact angle trend when depositing Al2O3 via ALD to modify thin-film composite polyamide reverse osmosis membranes using trimethylaluminiun and water as precursors. Briefly, they also observed an immediate decrease in water contact angle with ALD-Al2O3 treatment, but further increasing the number of cycles increased the water contact angle. This was partially attributed to the unreacted precursor on the membrane surface. In our study, a lower binding energy N 1s peak component, potentially attributed to TDMAT ligands, was not observed, suggesting that NP aggregation may play a primary role.

2.4. NP Nucleation and Growth Mechanism. Together, TEM, XPS, BET, AFM, and water contact angle results describe a nuanced nucleation and growth process for TiO2 on PDA. Specifically, as shown by TEM images of NP size distribution, the particles grow in a clearly nonlinear fashion (Figure 1). First, samples from the smallest ALD cycles (PDA/15ALD) showed the highest fraction of small NPs, and PDA/60ALD showed higher percentage of large NPs than PDA/15ALD and PDA/90ALD. Second, as expected, the increase of ALD cycles from 15 generated larger TiO2 particles in PDA/60ALD. Finally, the decrease in particle size as ALD cycle increased from 60 to 90 (sample PDA/60ALD and PDA/90ALD, respectively) may be attributed to further agglomeration of TiO2 nuclei on flexible PDA ligands, consequently encouraging nucleation on exposed active sites instead of secondary growth of existing TiO2 NPs.

With only 15 and 30 ALD cycles (PDA/15ALD and PDA/30ALD), TiO2 NPs nucleate and grow but remain below the detection limit of XPS. However, even with the minute amount of TiO2 on the surfaces, a noticeable decrease in the BET surface area (Figure 3) was observed. Upon further increasing ALD cycles, the resulting PDA/60ALD surface shows a rougher surface with higher water contact angle than the other PDA/ALD—TiO2 samples. The subsequent decrease in the Ti/F ratio, increasing titanium peak area, and increasing N 1s peak area for the PDA/90ALD samples indicate that NP aggregation occurs, exposing more neat membrane (fluorine containing) and dopamine-treated surface areas (N 1s containing) (Figure 3c). Decreased BET surface areas for the PDA/75ALD and PDA/90ALD samples, compared to the PDA/60ALD samples, indicate that NP aggregation and continued nucleation and growth not only reduced the total pore volume but also further smoothed the surface. As such, for the PDA-modified polymeric surfaces, the intriguing nucleation and growth mechanism may be exploited to enable drastic changes in membrane surface properties by depositing a small amount of TiO2 via ALD.

3. CONCLUSIONS

In this study, surface properties of commercial PVDF ultrafiltration membranes were altered using PDA followed by ALD of TiO2 in the nucleation and growth phase (<100 cycles) and compared to direct deposition onto PVDF without PDA. Nonlinearities in material properties were observed that may be carefully fine-tuned for desired surface properties in material design. Nonlinear trends are attributed to NP aggregation, but changes in the PDA structure and unreacted precursor could also play a role. Although ongoing research focuses on further clarifying the contribution of these three factors, mobility of NPs due to PDA flexibility may be primarily responsible for the nonlinear trends, based on XPS and nitrogen adsorption data. The versatility and biocompatibility of PDA and TiO2 render surface pretreatment with PDA followed by TiO2 deposition via ALD a feasible method for carefully engineering surface properties of many materials, although resultant properties will depend on the specific support structure and surface pretreatment conditions. A thorough, atomic or molecular level understanding of surface treatments with PDA and NPs may be rudimentary to many material optimizations such as improving the solubility of COFs and engineering textile surface properties through ALD.

4. EXPERIMENTAL SECTION

4.1. Materials. Synthet flat sheet PVDF ultrafiltration membranes (YMBN3001, 0.22 mm thickness) were purchased from Sterlitech Corporation. Dopamine hydrochloride was acquired from Sigma-Aldrich. Tris-HCl solution (pH = 8.5, 1.0 M) was purchased from Teknova Inc., and TDMAT from Sigma-Aldrich (99.999%) was used as received as the ALD precursor.

4.2. Membrane Wetting. All membranes were wetted with ethanol before PDA surface treatment. This process consisted of submersion in ethanol for 1 min followed by soaking in deionized (DI) water for 30 min.

4.3. Dopamine Polymerization. Tailoring dopamine deposition to a specific application is strongly dependent on dopamine concentration and deposition time because these parameters directly impact the PDA layer thickness and chain structure. Times of 3−24 h are commonly used with up to 5 days of polymerization in some cases. Additionally, a thorough analysis of the effect of dopamine concentration and polymerization time was recently reported by Kasemset et al., in which initial dopamine concentrations between 0.1 and 8 mg mL−1 and polymerization times between 15 and 240 min were investigated, with the highest pure water permeance being achieved with an initial concentration of 2 mg mL−1 and polymerization time of 15 min. As such, polymerization time greatly impacts material performance and needs to be carefully optimized for targeted applications. In this case, we used 15 min of dopamine polymerization to produce relatively short polymer chains.

Selected membranes were coated with PDA in a process consisting of several steps and closely following that used by Shao et al. Briefly, after ethanol pretreatment, membranes were soaked in Tris-HCl solution (pH = 8.5) for 5 min. This was followed by soaking the active side of the membrane in an aqueous dopamine solution (2 mg mL−1) for 24 h. The membrane was then rinsed with DI water to terminate polymerization and remove noncovalently bonded molecules. Membranes were continuously agitated on a Thermo Scientific test tube rocker during PDA coating.

4.4. ALD of Titanium Dioxide (ALD−TiO2) onto the Membrane Surface. Following dopamine treatment and/or ethanol wetting, TiO2 deposition was performed using an Ultratech/CNT Fiji F200 ALD system (Waltham, MA).
same substrates were modified with highly variable conditions, but not repeated. The ALD reactor was maintained at 1 × 10^{-5} Torr or better when idle and 1 × 10^{-1} Torr during TiO_2 deposition. TDMAT was utilized as the metal precursor and 18 M\Omega water was utilized as the oxygen source. The TDMAT precursor source was heated to 75 °C, whereas the water source was kept at room temperature. The precursor delivery lines and substrate were heated to 100 °C, with all temperatures stabilizing before the deposition was initiated. Argon (Ar) carrier gas was continuallyowing at a rate of 0.260 L min^{-1}, with one complete deposition cycle consisting of a 0.12 s pulse of TDMAT, 60 s purge with Ar, 0.06 s pulse of water, and 60 s purge with Ar. A summary of processing parameters for the ALD–TiO_2 membranes is included in Table 1. Membrane samples that were treated with PDA, followed by ALD–TiO_2, will be referred to as PDA/ALD–TiO_2. An ALD growth rate of 0.46 Å/cycle was estimated by performing ALD depositions onto silicon (100). The rate was measured by spectral reflectance using Filmetrics F20-UV and accompanying fitting software (Filmetrics, San Diego, CA).

The ALD deposition was optimized for 100 °C, based on thermogravimetric analysis (TGA) experiments, to avoid polymer degradation. Heat-induced changes to membrane morphology were examined by placing a membrane sample in the ALD chamber at the conditions used without depositing titanium onto the surface. AFM characterization was carried out for the heat-treated and neat PVDF membrane samples. Details of both TGA and AFM measurements are outlined in the Supporting Information, with results summarized in Figures S14 and S15. For experiments utilizing UV light to irradiate TiO_2 NPs, treated membranes were exposed to UV light using a 100 W OmniCure S2000 lamp for 10 min.

4.5. Membrane Characterization. SEM characterization was carried out using a FEI Quanta FEG 450 field emission scanning electron microscope equipped with a backscattered electron detector. Cross-sectional images were taken in the bulk membrane, between the support and active side to search for changes in the overall membrane structure. TEM/EDXS images were collected using a Hitachi H-7000 transmission electron microscope with an accelerating voltage of 75 kV. Fromvar/carbon square copper grids with 400 mesh from Electron Microscopy Sciences were used for all depositions (FCF400-CU-UA). AFM was performed in a noncontact ac mode (Oxford Instruments Asylum Research, Santa Barbara, CA). rms surface roughness values from 5 μm × 5 μm areas are reported. Water contact angles were measured using a Kruse EasyDrop system. Reported values are the average of five samples collected for each membrane type.

BET porosity measurements of treated and untreated membranes were carried out using nitrogen adsorption/desorption cycles at 77 K (Micromeritics ASAP 2020). All calculations were completed using Micromeritics ASAP 2020 software. The algorithms are described in the ASAP 2020 Operator’s Manual and are briefly described below.75

To begin calculation of the BET surface area, eq 1 is used to calculate the BET^2 transform for \( B_1 \) in units of g cm^{-3} STP for each data point.

\[
B_1 = \frac{P_{rel}}{(1.0 - P_{rel}) \times N_{adv}}
\]

The parameter \( P_{rel} \) is the unitless relative pressure between the absolute pressure and saturation pressure at a point, and \( N_{adv} \) represents the amount of gas adsorbed after equilibrating the dose and has units of cm^3 STP. From eq 1, the software calculates the slope (S, g cm^{-3} STP) and y-intercept (\( Y_{INT} \) g cm^{-3} STP) of the resulting line. These quantities can be combined with the analysis gas cross-sectional area (nm^2) to calculate the BET surface area using eq 2.

\[
S_{BET} = \frac{CSA \times (6.023 \times 10^{23})}{(22.414 \text{ cm}^3 \text{ STP}) \times \left(10^{18} \text{ nm}^2 \text{ m}^{-2}\right) \times (S + Y_{INT})}
\]

The BJH method calculates pore sizes using the Kelvin model of pore filling. First, the Kelvin core radius is calculated using eq 3.

\[
R_{K} = \frac{-A}{(1 + F)\ln(P_{rel})}
\]

In eq 3, \( A \) is the adsorbate property factor, \( F \) is the fraction of pores open at both ends, and \( P_{rel} \) is the relative pressure. The fraction of pores open at both ends is assumed to be zero for desorption. Further calculations account for the thickness of the adsorbed layer to yield an adjusted measurement of the pore size. Pore size distributions were calculated using BJH adsorption.

XPS measurements were obtained using Kratos Axis Ultra with a delay line detector with a monochromatic Al K\( \alpha \) X-ray source system (Kratos Analytical Manchester, UK). The X-ray source power of 60 W was chosen to minimize X-ray damage as sample discoloration was observed with higher X-ray power. Survey scans were collected with passing energy of 80 eV and dwell time of 500 ms per 0.10 eV. High-resolution scans were collected with passing energy of 40 eV with dwell times of 250–340 ms and represent an average of three scans. An onboard electron flood gun was employed to provide charge compensation for all measurements. When idle, the system was maintained at a vacuum of 5 × 10^{-10} Torr or lower. During measurements, the vacuum was maintained between 1 × 10^{-9} and 2 × 10^{-9} Torr. All spectra were shifted to align the C 1s peak attributed to saturated, unfunctionalized carbon to 284.5 eV.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00864.

- BET adsorption and desorption isotherms and TGA, AFM, and XPS results (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: dli1@uwyo.edu (K.D.L.-O.).

**ORCID**

Audra DeStefano: 0000-0003-1047-2637
Bruce A. Parkinson: 0000-0002-8950-1922
Katie Dongmei Li-Oakey: 0000-0002-0529-9203

**Notes**

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