Lawrence Berkeley National Laboratory

Recent Work

Title

Quantitative Characterization of a Desalination Membrane Model System by X-ray Photoelectron Spectroscopy.

Permalink

<https://escholarship.org/uc/item/6nc7t983>

Journal

Langmuir : the ACS journal of surfaces and colloids, 35(35)

ISSN

0743-7463

Authors

Buechner, Christin
Gericke, Sabrina M
Trotochaud, Lena
et al.

Publication Date

2019-09-01

DOI

10.1021/acs.langmuir.9b01838

Peer reviewed

Quantitative Characterization of a Desalination Membrane Model System by XPS

Christin Buechner¹, Sabrina M. Gericke¹, Lena Trotochaud^{1,§}, Osman Karshioğlu^{1,&}, Joseph Raso^{1,#}, Hendrik Bluhm^{1,2,§,}*

¹ Chemical Sciences Division and ²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

[§] Present address: Center for WaSH-AID, Duke University, Durham, NC 27708, USA

[&] Present address: Department of Interface Science and [§] Department of Inorganic Chemistry, Fritz-Haber-Institute of the Max-Planck-Society, D-14195 Berlin, Germany

[#] Present address: Department of Chemistry, University of Colorado, Boulder, CO 80304, USA

ABSTRACT

Aromatic polyamide films form the active layer in reverse osmosis (RO) desalination membranes. Despite widespread use of this technology, it suffers from low rejection rates for certain water contaminants and from membrane fouling. Through a better understanding of the fundamental surface chemical processes during reverse osmosis desalination, advances in membrane and material design are expected. The recent invention of a molecular layer-by-layer (mLbL) preparation technique¹ yields films that are sufficiently smooth to warrant investigation with high resolution microscopy and spectroscopy methods. We present high-resolution, quantitative XPS data on the surface chemistry of ultrathin polyamide films that can serve as a model system for

desalination membranes. We show that a quantitative analysis of the XPS spectra gives information on the functional groups of the film as well as other compounds present due to the synthesis under ambient conditions. Unpolymerized functional groups are identified and aid in understanding the degree of crosslinking. Investigation of polymers with synchrotron-based XPS requires taking beam induced changes into account. We quantify X-ray beam damage and show that beam damage to the polyamide is limited, allowing long-term investigation of thin polyamide films. Characterizing mLbL grown films in high-resolution XPS is the basis for a better understanding of the chemical interplay of polyamide surface functional groups with the major components of desalination systems.

INTRODUCTION

Seawater desalination by reverse osmosis (RO) provides freshwater for water-stressed regions, and is expected to become more important in the coming decades.² Current RO systems rely on an active layer of aromatic polyamide, most frequently produced by crosslinking trimesoyl chloride with m-phenylene diamine (sometimes called Poly(m-phenylenediamine trisamide), P(mPDTA)) that is a few 100 nm thick.³

Retention rates in RO vary depending on the contaminant type, but do not correlate with contaminant size.⁴ Instead, charged contaminants appear to be rejected most effectively,⁵ indicating that electrostatic interactions on the membrane surface influence the exclusion mechanism. A better understanding of chemical and electrostatic interactions between surface groups, water and contaminants is needed in order to tailor membrane materials towards respective applications. Interface science methods with high chemical and spatial resolution have been further

developed in recent decades to operate under increased relative humidity. One of these methods is X-ray photoelectron spectroscopy (XPS), which delivers insights into the chemical makeup of materials with high surface sensitivity. Commercial membranes, however, are not suitable for XPS investigation, due to the rough surface of the membranes, in conjunction with electrostatic charging due to limited electrical conductivity of bulk polymer samples.

Recently, a novel molecular layer-by-layer (mLbL) preparation technique was reported,¹ which allows producing polymer films on a substrate with monomer precision and tunable thickness. Choosing the same monomers as conventional desalination membranes,⁶⁻⁸ the mLbL approach yields systems that have comparable chemistry, but a smooth morphology that lends itself to fundamental studies of the liquid-solid interface chemistry. The resulting P(mPDPA) films, grown on Si wafers, were analyzed with XPS to show a high degree of crosslinking.¹ Atomic force microscopy shows that these films are 1-2 orders of magnitude smoother than commercial membranes. Furthermore, for very thin films, charge compensation is improved, thus reducing charge-induced shifts and peak broadening in XPS. Compared to vapor deposition or wash-and-rinse cycles of the monomers which can lead to dendritic growth,^{9,10} mLbL provides control over the growth process, as was shown from the observation of the development of film thickness with successive layers deposited.¹ The benchtop mLbL process also provides flexibility in terms of monomer choice and surface functionalization.^{11,12} Furthermore, this technique can be automated for producing multilayer films relatively quickly,¹³ while ensuring a smooth morphology. As the mLbL preparation is carried out under ambient conditions, possible contaminations from adventitious carbon sources need to be taken into account, as well as residual solvent and water in the films, if one is to make a quantitative assessment based on XPS.

Synchrotron-based XPS is ideally suited to study the reactivity of these films with water and common contaminants. Soft X-rays in particular can achieve high surface sensitivity, but have a 10-100 times higher photoionization cross section than the photons from Al- or Mg-lab-based sources.¹⁴ Hence, any beam induced changes to polyamide films need to be understood in order to obtain reliable insights from soft X-ray techniques, such as photoelectron spectroscopy,¹⁵ X-ray absorption spectroscopy¹⁶ or scanning transmission X-ray microscopy¹⁷⁻¹⁹ and others.²⁰ Typical covalent bonds in polymers can be dissociated with as little energy as an ultraviolet photon,²¹ but mechanisms of initiation, promotion and termination of photo-induced reactions strongly depend on the absorption at a given photon energy. Polymers generally exhibit many different pathways of degradation, and contaminants present in any given formulation contribute to the pattern of competing pathways.²¹ We show that XPS can be used to monitor chemical changes caused by X-rays and secondary electrons, as well as net mass loss of thin films.

In this report, we present data on monolayer P(mPDTA) films (shown schematically in Figure 1), prepared by previously reported mLbL spin coating deposition from bi- or trivalent monomers, on wafer substrates coated with Au and Pt, respectively.^{1,13} Peak assignments can be made in agreement with the literature and specific chemical groups reflect the degree of crosslinking in the films. Quantitative analysis of XPS data provides insight into the nature of adventitious carbon species and trapped water. In order to ensure the stability of the model system during prolonged investigation with XPS, beam induced changes in the films have been investigated in detail, and quantified with respect to photon flux. Beam induced decomposition pathways are in line with results reported for other amide materials.

Figure 1. Schematic representation of the preparation of aromatic amide monolayer on a metal substrate.¹ Two monomers are sequentially deposited, repeating the deposition adds further layers. The four different carbon functional groups of the product are color-coded in reference to the peak assignments in the C 1s XPS spectrum (cp. Figure 2). The structure also contains two distinct nitrogen species and two distinct oxygen species.

EXPERIMENTAL DETAILS

Film preparation

Samples were prepared as follows, in agreement with published procedures.^{1,13} Substrates consisting of Au- and Pt-coated wafers were cleaned from organic residues in an oxygen plasma etcher. Using a spin-coater, substrates were covered with a 1% solution of monomer A in toluene, and the excess subsequently rinsed with toluene. The sample was then covered with a 1% solution of monomer B in toluene, and rinsed with acetone. For monomer A, either trimesoyl chloride (denoted A3 for its 3 functional groups) or terephthaloyl chloride (A2) were used as purchased. Using A3 results in the formation of crosslinks, while A2 can only form linear polymer chains.

For monomer B, m-phenylene diamine (denoted B2) was used as purchased (see Figure 1 and Supporting Information Figure S1 for the chemical structures of the monomers). This protocol allows building up aromatic amides in a layer-by-layer fashion, as previously reported.^{1,13} To remove any excess solvents, samples were dried at 60 °C in a vacuum oven for 12 h.

XPS measurements

The samples were mounted with stainless steel clips onto a ceramic button heater and introduced into a vacuum chamber at $\sim 10^{-10}$ Torr. The mounting clips also provided the electrical connection of the sample surface to ground. Prior to the XPS experiments, the samples were heated to 60 °C in UHV to decrease the amount of water adsorbed on or in the film during their exposure to air.

XPS spectra were taken using the APXPS-1 endstation (ambient pressure X-ray photoelectron spectroscopy) at Beamline 11.0.2 at the Advanced Light Source in Berkeley,²² with a modified Specs Phoibos 150 analyzer. The combined beamline and analyzer resolution was better than 0.35 eV. Photon energies of 490 eV were used for C 1s spectra as well as for Pt 4f spectra, 600 eV for N 1s spectra and 735 eV for O 1s spectra. While the endstation can tolerate pressures in the few Torr-range, the data shown in this report were recorded at pressures $< 10^{-7}$ Torr.

Beam induced changes are a common issue in analyzing polymers and other materials based on lighter elements. We quantified the changes that occur in each particular core level spectrum with exposure to X-rays over time, and find a universal beam damage behavior, when controlling for absolute photon exposure. Photon exposure was calibrated with a Opto Diode AXUV100G photodiode. Full flux corresponds to 4×10^7 photons $\text{s}^{-1} \mu\text{m}^{-2}$ at 735 eV. In order to study beam damage as a function of photon flux per second, the undulator gap of the beamline was detuned to reduce the photon flux to 10% or 33% flux of the nominal value.

Data analysis

Due to the possibility of the polymer charging by an unpredictable amount, the binding energy (BE) scale for all spectra was calibrated to the main C 1s peak at 284.7 eV.²³ The spectra were fit with linear or Shirley backgrounds, Voigt peak shapes (for C 1s, O 1s, N 1s) or Donjiach Sunjich doublets (for Au 4f, Pt 4f), using the KolXPD software package. The spectra shown in this manuscript are representative for the 5 samples (2 on Pt-covered substrate, 3 on Au-covered substrate), and were each measured on at least 3 different sample positions, to ensure reproducibility.

RESULTS AND DISCUSSION

Peak assignment

Core level spectra of a 1ML film with monomers A3 and B2, prepared on a wafer coated with a 7 nm thick layer of Pt are shown in Figure 2. Survey spectra show carbon, oxygen, nitrogen, and metal substrate species (Au or Pt). No Cl residue from the precursor was observed in surveys, nor any other elements. High resolution spectra of the polymer film core levels were taken with a kinetic energy of 200 eV to provide surface sensitive information. Peak assignments are made based on reported binding energies in the literature and are described in the following section. Furthermore, the respective peak areas and behavior of each species under the X-ray beam provide corroboration for the peak assignments and further insight, and are discussed in the following sections.

The Pt 4f spectrum shows two doublets, with the Pt 4f_{7/2} signal at 70.8 eV, i.e. in the energy range for elemental Pt, while a second component, shifted by 0.7 eV to higher BE, indicates a partially oxidized surface species.²⁴ In the case of a gold-coated substrate, we observe a Au 4f doublet with the Au 4f_{7/2} component at 84.0 eV which is characteristic for metallic Au.²⁵

The O 1s spectrum consists of two components, which exhibit different intensities, depending on the film thickness and experimental conditions, but are always located at the same peak positions. The O 1s spectrum shown in Figure 2 is representative for films of 1 ML thickness. The low BE feature is typically located at 531.2 (± 0.2) eV, which is in good agreement with binding energies recorded for aromatic amides.^{23,26,27}

The second feature is typically shifted by 1.4 eV to a binding energy of 532.6 (± 0.3) eV. Several chemical species have binding energies in this region: i) OH groups present in unlinked COOH-groups of monomer A, ii) OH groups present in adventitious carbon, iii) a shake-up feature which could amount to almost 10% of the low-BE peak area²³ and, iv) trapped water in the film.²⁶ The assignment of the high-BE O 1s peak will be discussed in more detail below in the context of a quantitative analysis of peak areas.

The C 1s spectra show 4 peaks, at 284.7 (± 0.02) eV (green trace), 285.8 (± 0.1) eV (blue) and 287.3 (± 0.2) eV (pink), as well as a very small feature at 288.4 (± 0.5) eV (cyan). From low to high BE, the peaks can be assigned to i) C-C bonds in the benzyl rings, ii) a peak with contributions from C-N groups in monomer B as well as OH-groups either formed on the polymer or present in adventitious carbon compounds, iii) the carbon atoms in amide groups and iv) the carbon atoms in unlinked COOH-groups of monomer A.^{23,26,27} A very small shake-up feature can be identified in the range of 291-292 eV (not shown).^{23,27,28}

The N 1s spectrum is dominated by a single peak, which exhibits a small shoulder at lower binding energy. The main signal with BE 399.7 eV is assigned to the amide nitrogen group,^{10,23,28} while the one at 398.5 eV is assigned to the terminating NH₂-groups at the polymer/gas phase interface.²⁹

The peak assignment shows that the ultrathin amide film contains the chemical functionalities (amide, carboxylic acid, amine) that have been shown to govern the mechanism of water transport in reverse osmosis membranes.³⁰

Figure 2. XPS spectra of Pt 4f, O 1s, C 1s, and N 1s core levels of a 1 ML aromatic amide film with peaks assigned to likely chemical moieties.

Quantitative analysis

Comparing relative peak areas within and across spectra can provide further insights into the sample composition, especially for C 1s and O 1s, where different chemical species have overlapping binding energies. For the following analysis, we refer to the spectra shown in Figure 2, while the general insights are representative across samples (see Supporting Information for fitting parameters and raw data).

Based on previous reports,¹ the mLbL technique is expected to yield a highly crosslinked film. The stoichiometry between oxygen and nitrogen in amide films observed by XPS is frequently used to determine the degree of crosslinking, with a ratio of 1 indicating a fully crosslinked system. However, there are several factors that can distort this correlation, and need thus to be taken into account. Contributions from unpolymerized groups terminating the chain will have a strong effect on the stoichiometry for very thin films, but will fall within the standard deviation somewhere between 5 and 10 repeat units. Furthermore, the nature of the anchoring site is not fully understood and may vary when the substrate material is changed, hence, any chemical group involved in linking the film to the substrate will skew the stoichiometry in very thin films. Due to the preparation of mLbL films under ambient conditions, the presence of additional material is also very likely. Contamination resulting from, e.g., handling samples with disposable gloves, such as Si or S, can be detected in survey spectra if they are present at concentrations of a few percent of a monolayer or more.³¹ Adventitious carbon from atmospheric volatile organic compounds^{32,33} are also expected to contribute intensity to C 1s and O 1s spectra and are often difficult to quantify. In addition, toluene and acetone are used during the sample preparation, potentially leaving residues. Furthermore, trapped water has been observed even in few-nm thick films.²⁶ Since many of these compounds have C 1s and O 1s binding energies overlapping with the species present in the

aromatic amide, a fully quantitative analysis of the observed peak areas is outside the scope of this study. By comparing the areas of corresponding peaks across core levels, however, we can identify likely candidates for those contaminants.

Despite these confounding factors, the chemical resolution of XPS allows quantifying the specific chemical groups that are present in incompletely crosslinked systems. These groups are an amine group and a free acid group, respectively. The amine group is well separated as a low BE shoulder in the N 1s spectrum, accounting for almost $\frac{1}{4}$ of the total peak area. Amine groups from unpartnered monomers contribute to this shoulder. In the case of a 1-layer film discussed here, however, the shoulder is dominated by the amine groups terminating the surface and not meaningful for extracting a value for crosslinking density. The COOH group can be identified in the C 1s spectrum as a small high BE peak accounting for about 3% of all carbon atoms, or 15% of the oxygenated carbon atoms. Besides unpolymerized groups from the original monomer A which have hydrolyzed, no other species are expected to contribute to this C 1s peak at 288.4 eV. We can therefore conclude that only a small number of the monomer A linkers fail to bind to a monomer B amine group, yielding a film of 85% crosslinking density. In a recent study, the absolute concentration of acid groups was quantified using FTIR,³⁴ and it was found that it is highest for very thin films.

From a careful analysis of relative peak areas in the C 1s spectrum and referencing the stoichiometry of the molecule (see Figure 1), we can draw conclusions about additional contributions to the C 1s spectrum, which can later be corroborated by comparing different core level spectra. For an ideal, fully crosslinked polyamide system, there should be equal amounts of C-N atoms (contributing to the blue peak in Figure 2) and C=O atoms (contributing to the pink and cyan peaks). Assuming that one side group of monomer A binds to the substrate, the remaining

two acyl chloride groups could react with two molecules of monomer B. As seen in Figure 1, each monomer B contains a second linker which is terminating the chain in the case of a 1 ML film, resulting in a theoretical N/O ratio of 4/3. We find, however, that the C-N peak can be two times larger than the two high BE peaks in the case of platinum substrates, and up to three times larger in the case of gold substrates. The difference between substrate materials could stem from a chemical affinity of a preferential binding of amines on gold, which would lead to a partial displacement of monomer A by monomer B and has been suggested in other work.³⁴

For either substrate, the unexpectedly high relative peak area around 286 eV is likely due to additional chemical species contributing to the C-N peak. We can corroborate this assumption by comparing areas in C 1s core level spectra with corresponding O 1s and N 1s spectra. The peaks fitted in Figure 2 are color-coded to show how the same functional group is reflected in different core-level spectra, for instance the amide group contributes to the carbonyl peak in the O 1s spectrum, the main peak in the N 1s spectrum, and to two peaks in the C 1s spectrum, all of which have a pink trace. Calibrating the instrument with CO₂, O₂ and N₂ gas phase spectra, we obtain relative sensitivity factors for C, O and N specific for our experimental chamber. Using these factors, we can quantitatively compare the peak areas across spectra which have a peak assigned to the same species. We find indeed that the overall area in the N 1s spectrum is smaller than expected based on the C-N peak in the C 1s spectrum, but fits the expected value when extrapolated from the C 1s oxygenated species and the molecule stoichiometry. This is an indication that adventitious carbon species contribute to the C-N peak area.

This interpretation is further corroborated by correlating the COOH- and the amide peak with peak areas in the O 1s region. Assuming only the aromatic amide to be present, the pink peak at 287.3 eV (Fig. 2) is assigned to the amide functional group (containing one oxygen in a C-O double bond)

and the cyan peak at 288.4 eV is assigned to unpolymerized carboxylic acid groups (containing one oxygen atom in double and single-bonded situations, respectively). From the area of these peaks, the assumed stoichiometry and the known sensitivity factor, we can determine an expected peak area for the entire O 1s region, as well as the peak connected with O doubly-bonded to carbon. Comparing these expected areas to the observed areas for several samples, we find that the overall intensity in the O 1s spectrum exceeds the expected value, sometimes only by a fraction, but in other cases by a factor of 2-5. A shake-up feature that would be observed under the high-BE peak in the O 1s spectrum can only account for a discrepancy of 10%.²³ This is a strong indication for the presence of additional species contributing to the oxygen spectrum. Since the survey spectrum does not reveal any additional elements other than O, C, N and the substrate metal, it is likely that adventitious carbon containing OH/OR functional groups, water or OH groups on the substrate contribute this additional intensity to the O 1s region. OH groups in adventitious carbon molecules would have a binding energy in the region of 286 eV of the C 1s spectrum,²³ which is consistent with the excess area that is observed in that energy region.

The presence of alkoxy-groups in adventitious carbon is suggested by quantitative analysis of the C 1s spectrum, as well as comparisons across all core level spectra. It is also consistent with beam induced changes, as we will discuss in the following section.

Beam damage evaluation

Investigating polymer samples with X-rays, especially from a highly brilliant light source such as an undulator beamline at a 3rd generation synchrotron, can cause photon-induced changes to the sample, also known as beam damage. The extent of beam damage is dependent on the excitation

energy, incident photon flux and the cumulative photoionization cross sections for all elements in the sample at the given photon energy, and therefore has to be determined under the experimental conditions relevant for each investigation. In the case of polyamide films on Au- or Pt-coated substrates, O 1s has the highest binding energy out of all the core levels involved. Hence, for studies probing over either many sample positions or incident angles, the full set of core levels (O 1s, C 1s, N 1s) will be probed with 735 eV excitation energy, allowing for faster measurements. We therefore investigate the effects of prolonged exposure of the same sample position to 735 eV X-rays. Analyzing the overall peak area in the core level spectra, and the decreases or increases of peaks at each binding energy can provide insights into the beam-induced changes. A decrease in the total peak area of a given core level is generally interpreted as mass loss of that element, while changes in the relative peak intensities indicate chemical changes in the sample.

Since a variety of chemical moieties are present on the surface, it is likely that a number of chemical degradation pathways occur when the sample is exposed to X-rays. Schematic 1 lists reactions that likely follow photoionization,^{35,36} and suggests possible reaction products. Each of those hypothetical pathways would affect the peak areas differently, allowing us to compare to observed beam induced changes and to identify the most dominant pathways.

Scission events can lead to the loss of OH/OR groups, causing a net intensity loss in O 1s and shifts to lower binding energy in C 1s. Species under the high BE C 1s peaks could include COOH, (C=O)R, RO-C-OR. The latter can undergo scission to a COR, contributing to the C 1s peak growth at 286 eV and O 1s peak loss around 533 eV, or undergo scission and desaturate to a C=O, contributing to the 288eV C 1s peak while in turn increasing the O 1s C=O peak and decreasing the OR peak. Amide groups can undergo scission and result in CN triple bonds,³⁶ contributing to

growth around 286-287 eV in the C 1s spectrum, as well as shifting some of the intensity in the N 1s spectrum to lower binding energy.

				C1s spectrum				O1s spectrum		N1s spectrum	
	change	groups affected	remaining functional group	284.7	285.8	287.3	288.4	531.2	532.9	398.5	399.7
Polyamide	OH scission	(C=O)-OH	aldehyde, crosslinked ketone			↑	↓		↓		
	carbonyl-O scission	(C=O)-NH, (C=O)-OH	imine, nitrile, cross-links	↑	↑	↓	↓	↓			↓
other species	OR scission	RO-C-OR	C-OR, C=O		↑	↓		↑	↓		
	OH scission	R-OH	hydrocarbon	↑	↓				↓		
	evaporation	H ₂ O, OH (recombined)							↓		

Schematic 1. Hypothetical pathways of beam damage, laying out affected chemical groups and resulting species. Peak positions are color coded in reference to Figure 2. Arrows indicate resulting changes in peak intensity.

For the ultrathin polyamide films employed in this study, beam damage in ultrahigh vacuum exhibits reproducible behavior across several samples. Different flux settings were tested, to discover any dependency of the deterioration on photon flux and exposure time. The X-ray doses for the beam damage study were chosen to be equal to or larger than the typical dose that samples are exposed to for time-intensive angle-resolved studies or typical APXPS measurements. All data show consistent beam damage trends when normalized for absolute radiation dose rate (i.e. photons/(area*time)). Figure 3 shows representative spectra for a 1 ML polyamide film on a Pt-coated substrate, exposed to X-rays at 10% of normal flux for 3 hours (see Supporting Information Figure S3 for peak intensity plotted over time).

For the C 1s spectrum, the total peak area stays constant over the course of the exposure. We observe that the two peaks at higher BEs significantly lose intensity, which is consistent with the general pattern of oxygenated carbon species being most susceptible to beam damage.^{21,23,35} Both peaks show a similar decay curve, with steep initial intensity losses and subsequent stabilization at 50% of the original peak area. The peak around 286 eV increases in intensity by about the same amount, while the peak around 285 eV shows no significant change. This pattern is consistent with C-(OR)₂ bond scissioning to form C-OR moieties.²³

No mass loss is observed in the N 1s spectrum, but about 15% of the main peak area shift to slightly lower binding energy, consistent with C-N triple bond formation. This would technically require adding a new peak by around 0.3 eV lower than the amide peak position, but that is below the resolution of this experiment. This is the most direct indication that the aromatic amide is affected by beam damage, but also shows that damage is limited even for prolonged exposure, and the majority of the amide model film is preserved during beam damage experiments.

In the O 1s spectra, an overall mass loss of 35% is observed throughout the beam damage series. That loss is observed in the high BE peak, which is comprised of adventitious carbon, excess water and OH groups, as well as the OH function in unpolymerized COOH-groups. The low BE peak shows a very slight increase in the first 30 minutes of X-ray exposure.

Figure 3. C 1s (top) and O 1s (bottom) spectra of pristine PA film (black trace) and film exposed to X-ray beam (red trace). Arrows indicate characteristic changes in peak areas that were consistently observed.

Since the C 1s spectrum shows no loss in the integrated intensity, while the O 1s spectrum does, we can determine that most of the lost material originates from oxygen present in the sample from water, substrate OH groups or adventitious carbon sources, rather than the amide film itself. The fact that the decay curves for the two high-BE peaks in C 1s attenuate while about half of the initial

intensity remains indicates that while some species suffer from beam induced changes, other species stay intact. This pattern is consistent with adventitious carbon suffering the most damage, while the aromatic rings in the amide protect the molecules from significant damage, as was shown in an X-ray absorption study with 10x higher photoionization cross section.^{14,35}

Conclusions

We present synchrotron-based XPS spectra of a monolayer of aromatic amide grown by mLbL. Synchrotron based spectroscopy of these samples is challenging, due to the preparation under ambient conditions introducing unknown contamination and increased beam damage when soft X-rays are used. We use a multi-step approach to gain insights into the chemical composition of the sample. We study high-resolution XPS spectra to identify the binding energies of species present on the sample, which can be assigned to the aromatic polymer as well as a range of additional compounds. The presence of specific chemical groups can be used to deduce incomplete polymerization and degree of crosslinking. We use quantitative analysis to compare the peak areas of different core level spectra to confirm the presence of water, OH groups, and the likely nature of adventitious carbon compounds. These assumptions are corroborated by discussing the shifts in peak intensities that occur during exposure to X-rays.

This study provides the basis for investigating mLbL films of aromatic amides in the context of water purification. By harnessing the capabilities of ambient pressure X-ray photoelectron spectroscopy, the chemical interplay of the polymer, water and common contaminants can be understood at the molecular level, thus facilitating improvements in membrane rejection and surface fouling.

Acknowledgement

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences of the US Department of Energy under Contract No. DE-AC02-05CH11231. The ALS and the MES beamline 11.0.2 are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy at the Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231. C.B. is grateful for support from the Alexander von Humboldt Foundation through a Feodor Lynen Research Fellowship. S.G. is grateful for support from a PROMOS scholarship provided by the Freie Universität Berlin.

Supporting Information.

The following files are available free of charge.

Details regarding data fitting and beam damage (PDF)

AUTHOR INFORMATION

Corresponding Author

*bluhm@fhi-berlin.mpg.de

REFERENCES

- (1) Johnson, P. M.; Yoon, J.; Kelly, J. Y.; Howarter, J. A.; Stafford, C. M. Molecular Layer-by-Layer Deposition of Highly Crosslinked Polyamide Films. *J. Polym. Sci. Part B Polym. Phys.* **2012**, *50* (3), 168–173. <https://doi.org/10.1002/polb.23002>.

- (2) Karatairi, E.; Darling, S. B. Crises and Opportunities at the Energy-Water Interface. *MRS Bull.* **2018**, *43* (6), 404–405. <https://doi.org/10.1557/mrs.2018.129>.
- (3) Greenlee, L. F.; Lawler, D. F.; Freeman, B. D.; Marrot, B.; Moulin, P. Reverse Osmosis Desalination: Water Sources, Technology, and Today's Challenges. *Water Res.* **2009**, *43* (9), 2317–2348. <https://doi.org/10.1016/j.watres.2009.03.010>.
- (4) Geise, G. M.; Lee, H.-S.; Miller, D. J.; Freeman, B. D.; McGrath, J. E.; Paul, D. R. Water Purification by Membranes: The Role of Polymer Science. *J. Polym. Sci. Part B Polym. Phys.* **2010**, *48* (15), 1685–1718. <https://doi.org/10.1002/polb.22037>.
- (5) Kartinen Jr., E. O.; Martin, C. J. An Overview of Arsenic Removal Processes. *Desalination* **1995**, *103* (1–2), 79–88. [https://doi.org/10.1016/0011-9164\(95\)00089-5](https://doi.org/10.1016/0011-9164(95)00089-5).
- (6) Cadotte, J. E. Reverse Osmosis Membrane. 4039440, 1977.
- (7) Cadotte, J. E.; Petersen, R. J.; Larson, R. E.; Erickson, E. E. A New Thin-Film Composite Seawater Reverse Osmosis Membrane. *Desalination* **1980**, *32*, 25–31. [https://doi.org/10.1016/S0011-9164\(00\)86003-8](https://doi.org/10.1016/S0011-9164(00)86003-8).
- (8) Schaefer, A.; Fane, A.; Waite, T. *Nanofiltration*; Elsevier Science, 2004.
- (9) Zhou, H.; Toney, M. F.; Bent, S. F. Cross-Linked Ultrathin Polyurea Films via Molecular Layer Deposition. *Macromolecules* **2013**, *46* (14), 5638–5643. <https://doi.org/10.1021/ma400998m>.
- (10) Steiner, Z.; Miao, J.; Kasher, R. Development of an Oligoamide Coating as a Surface Mimetic for Aromatic Polyamide Films Used in Reverse Osmosis Membranes. *Chem.*

- Commun.* **2011**, 47 (8), 2384–2386. <https://doi.org/10.1039/C0CC04379F>.
- (11) Choi, W.; Gu, J.-E.; Park, S.-H.; Kim, S.; Bang, J.; Baek, K.-Y.; Park, B.; Lee, J. S.; Chan, E. P.; Lee, J.-H. Tailor-Made Polyamide Membranes for Water Desalination. *ACS Nano* **2015**, 9 (1), 345–355. <https://doi.org/10.1021/nn505318v>.
- (12) Ismail, A. F.; Padaki, M.; Hilal, N.; Matsuura, T.; Lau, W. J. Thin Film Composite Membrane — Recent Development and Future Potential. *Desalination* **2015**, 356, 140–148. <https://doi.org/10.1016/j.desal.2014.10.042>.
- (13) Chan, E. P.; Lee, J.-H. H.; Chung, J. Y.; Stafford, C. M. An Automated Spin-Assisted Approach for Molecular Layer-by-Layer Assembly of Crosslinked Polymer Thin Films. *Rev. Sci. Instrum.* **2012**, 83 (11), 114102. <https://doi.org/10.1063/1.4767289>.
- (14) Yeh, J. J.; Lindau, I. Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters: $1 \leq Z \leq 103$. *At. Data Nucl. Data Tables* **1985**, 32 (1), 1–155. [https://doi.org/10.1016/0092-640X\(85\)90016-6](https://doi.org/10.1016/0092-640X(85)90016-6).
- (15) Zubavichus, Y.; Fuchs, O.; Weinhardt, L.; Heske, C.; Umbach, E.; Denlinger, J. D.; Grunze, M. Soft X-Ray-Induced Decomposition of Amino Acids: An XPS, Mass Spectrometry, and NEXAFS Study. *Radiat. Res.* **2004**, 161 (3), 346–358. <https://doi.org/10.1667/RR3114.1>.
- (16) Johnson, P. S.; Cook, P. L.; Liu, X.; Yang, W.; Bai, Y.; Abbott, N. L.; Himpsel, F. J. Imide Photodissociation Investigated by X-Ray Absorption Spectroscopy. *J. Phys. Chem. B* **2012**, 116 (24), 7048–7054. <https://doi.org/10.1021/jp3003596>.
- (17) Wang, J.; Morin, C.; Li, L.; Hitchcock, A. P.; Scholl, A.; Doran, A. Radiation Damage in

- Soft X-Ray Microscopy. *J. Electron Spectros. Relat. Phenomena* **2009**, *170* (1–3), 25–36.
<https://doi.org/10.1016/j.elspec.2008.01.002>.
- (18) Wang, J.; Botton, G. A.; West, M. M.; Hitchcock, A. P. Quantitative Evaluation of Radiation Damage to Polyethylene Terephthalate by Soft X-Rays and High-Energy Electrons. *J. Phys. Chem. B* **2009**, *113* (7), 1869–1876. <https://doi.org/10.1021/jp808289e>.
- (19) Beetz, T.; Jacobsen, C. Soft X-Ray Radiation-Damage Studies in PMMA Using a Cryo-STXM. *J. Synchrotron Radiat.* **2003**, *10* (3), 280–283.
<https://doi.org/10.1107/S0909049503003261>.
- (20) Liu, X.; Yang, W.; Liu, Z. Recent Progress on Synchrotron-Based In-Situ Soft X-Ray Spectroscopy for Energy Materials. *Adv. Mater.* **2014**, *26* (46), 7710–7729.
<https://doi.org/10.1002/adma.201304676>.
- (21) Mark, J. E. *Physical Properties of Materials, Second Edition*; CRC Press, 2011.
<https://doi.org/10.1201/9781439895320>.
- (22) Frank Ogletree, D.; Bluhm, H.; Hebenstreit, E. D.; Salmeron, M. Photoelectron Spectroscopy under Ambient Pressure and Temperature Conditions. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **2009**, *601* (1–2), 151–160. <https://doi.org/10.1016/j.nima.2008.12.155>.
- (23) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*; Wiley-VCH, 1992.
- (24) Butcher, D. R.; Grass, M. E.; Zeng, Z.; Aksoy, F.; Bluhm, H.; Li, W.-X. X.; Mun, B. S.;

- Somorjai, G. A.; Liu, Z. In Situ Oxidation Study of Pt(110) and Its Interaction with CO. *J. Am. Chem. Soc.* **2011**, *133* (50), 20319–20325. <https://doi.org/10.1021/ja207261s>.
- (25) Powell, C. J. J. Recommended Auger Parameters for 42 Elemental Solids. *J. Electron Spectros. Relat. Phenomena* **2012**, *185* (1–2), 1–3. <https://doi.org/10.1016/j.elspec.2011.12.001>.
- (26) Russat, J. Characterization of Polyamic Acid/Polyimide Films in the Nanometric Thickness Range from Spin-Deposited Polyamic Acid. *Surf. Interface Anal.* **1988**, *11* (8), 414–420. <https://doi.org/10.1002/sia.740110803>.
- (27) Kruse, A.; Thümmeler, C.; Killinger, A.; Meyer, W.; Grunze, M. X-Ray Photoemission Studies on Vapour-Phase-Deposited Polyamide Films. *J. Electron Spectros. Relat. Phenomena* **1992**, *60* (3), 193–209. [https://doi.org/10.1016/0368-2048\(92\)80042-7](https://doi.org/10.1016/0368-2048(92)80042-7).
- (28) Schmitz, C. H.; Schmid, M.; Gärtner, S.; Steinrück, H.-P.; Gottfried, J. M.; Sokolowski, M. Surface Polymerization of Poly(p -Phenylene-Terephthalamide) on Ag(111) Investigated by X-Ray Photoelectron Spectroscopy and Scanning Tunneling Microscopy. *J. Phys. Chem. C* **2011**, *115* (37), 18186–18194. <https://doi.org/10.1021/jp202986r>.
- (29) Graf, N.; Yegen, E.; Gross, T.; Lippitz, A.; Weigel, W.; Krakert, S.; Terfort, A.; Unger, W. E. S. XPS and NEXAFS Studies of Aliphatic and Aromatic Amine Species on Functionalized Surfaces. *Surf. Sci.* **2009**, *603* (18), 2849–2860. <https://doi.org/10.1016/j.susc.2009.07.029>.
- (30) Song, Y.; Xu, F.; Wei, M.; Wang, Y. Water Flow inside Polamide Reverse Osmosis Membranes: A Non-Equilibrium Molecular Dynamics Study. *J. Phys. Chem. B* **2017**, *121*

- (7), 1715–1722. <https://doi.org/10.1021/acs.jpcc.6b11536>.
- (31) Plasencia, A.; Strohmeier, B. R.; Piasecki, J. D. XPS Surface Characterization of Disposable Laboratory Gloves and the Transfer of Glove Components to Other Surfaces. *Spectroscopy* **2012**, 27 (7).
- (32) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; et al. Organic Aerosol and Global Climate Modelling: A Review. *Atmos. Chem. Phys.* **2005**, 5 (4), 1053–1123. <https://doi.org/10.5194/acp-5-1053-2005>.
- (33) Seinfeld, J. H.; Pankow, J. F. ORGANIC ATMOSPHERIC PARTICULATE MATERIAL. *Annu. Rev. Phys. Chem.* **2003**, 54 (1), 121–140. <https://doi.org/10.1146/annurev.physchem.54.011002.103756>.
- (34) Zimudzi, T. J.; Feldman, K. E.; Sturnfield, J. F.; Roy, A.; Hickner, M. A.; Stafford, C. M. Quantifying Carboxylic Acid Concentration in Model Polyamide Desalination Membranes via Fourier Transform Infrared Spectroscopy. *Macromolecules* **2018**, 51 (17), 6623–6629. <https://doi.org/10.1021/acs.macromol.8b01194>.
- (35) Coffey, T.; Urquhart, S. .; Ade, H. Characterization of the Effects of Soft X-Ray Irradiation on Polymers. *J. Electron Spectros. Relat. Phenomena* **2002**, 122 (1), 65–78. [https://doi.org/10.1016/S0368-2048\(01\)00342-5](https://doi.org/10.1016/S0368-2048(01)00342-5).
- (36) Johnson, P. S.; Cook, P. L.; Liu, X.; Yang, W.; Bai, Y.; Abbott, N. L.; Himpsel, F. J. Universal Mechanism for Breaking Amide Bonds by Ionizing Radiation. *J. Chem. Phys.* **2011**, 135 (4). <https://doi.org/10.1063/1.3613638>.

Table of Content graphic