Electronic supplementary information (ESI)

Chemical Communications

Development of an oligoamide coating as a surface mimetic for aromatic polyamide films used in reverse osmosis membranes

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A. Detailed experimental procedures used in the study

Chemicals.

Preparation of Gold Coated Silicon Wafers. Gold-coated silicon surfaces were prepared by coating silicon wafers (one side polished, 330-μm thick) with 10 nm titanium (99.995%, Kurt J. Lesker) followed by 30 nm gold (99.999%, Kurt J. Lesker) by evaporation. Both metals were evaporated thermally at a pressure equal to 2×10^{-6} bar using a thermal evaporator (Odem Ltd., Rehovot, Israel). Prior to coating, the silicon substrates were cleaned in acetone, then methanol, and then isopropanol in an ultrasonic bath (Bendeline Sonorex, London, England). Next, these were subjected to oxygen plasma cleaning for 5 min (0.4 mbar of oxygen pressure in chamber).

Contact Angle Measurements. Static contact angle of water under air for the different SAMs was measured using OCA 20 (Dataphysics Products, Filderstadt, Germany). Water drop size was 0.3 μL. At least four measurements were taken for each sample. The contact angle was extracted by SCA 20 software.

X-Ray Photoelectron Spectroscopy (XPS). XPS measurements were performed with an ESCALAB 250 (Thermo Fisher Scientific Inc., Waltham, UK) using an Al x-ray source and a monochromator. General survey spectra and high-resolution spectra of elements were recorded. Binding-energy measurements for the elements were corrected for the charging effect with reference to the C1s peak at 284.6 eV.

Ellipsometry. Film thickness of the formed organic phase was measured using an SE800 ellipsometer (Sentech Instruments GmbH, Berlin, Germany) on gold coated silicon wafers. Light spot size was 0.5 cm^2. Δ, the phase difference between the s and p polarized waves and Ψ, the amplitude attenuation, were measured as a function of the wavelength from 380nm to 820nm at incidence angles of 60˚, 65˚ and 70˚. The optical constants n and k of the underlying layers as a function of wavelength were calculated according to a measurement on a clean gold coated silicon wafer. This calculation was used as a substrate upon which we calculated the thickness of the organic layer by Cauchy's equation under the assumptions k=0, n_0=1.5, n_1=20. Refraction index of the organic layer was assumed to be 1.5 since direct measurements of the refraction index are not possible for such thin layers.

Synthesis of dendritic oligoamide film on gold surfaces. Prior to self-assembly, the gold-coated silicon wafers were cleaned twice for 10 min in an ultrasonic bath in toluene, acetone and ethanol. The

wafers were then dried with N_2 gas and placed in an ozone generator (Bioforce Nanosciences, Ames, IA) for 30 min. After cleaning, the wafers were immersed in 1 mM cysteamine in ethanol solution for 24 h at room temperature. At the end of the immersion step, the wafers were washed with ethanol, dried in N_2 gas and stored in a dry box.

The following steps of the synthesis were all done in one glass vial. It is imperative to first oven dry all glassware to prevent any reactions between water and 1,3,5-benzenetricarbonyl trichloride (TMC). If the self assembly was performed with the chloride salt of cysteamine, the amine charge should first be neutralized by adding 1% triethylamine in DMF, moderate shake for 10 min. This step is not needed if using neutral cysteamine.

To begin the syntheses wash the wafer and the vial with dichloro methane (DCM). Add 1 mM TMC in DCM solution. Drip triethylamine in DCM to a final concentration of 1.1 mM; shake mildly for 15 min. At the end of this stage, wash twice with DCM and dimethylforamide (DMF). Add 10 mM m-phenylenediamine (MPD) in DMF; shake mildly for 15 min. Wash with DMF at the end of this stage. Repeat this set of reactions for the production of another polyamide layer. The term cycle in this manuscript refers to the reaction with TMC followed by reaction with MPD. Half a cycle refers to a reaction with TMC only.

To terminate the reaction soak the wafer in water for 10 min, wash with ethanol and dry with N_2.

Table S1: Surface elemental composition of wafers coated by oligoamide films and of brackish water RO membrane type LE (by FILMTEC, Dow Water Solutions), as measured by XPS.

Surface type	**Au**	**S**	**Cl**	**O**	**C**	**N**
Cysteamine	23.9%	3.1%	1.8%	10.9%	57.2%	3.1%
1 cycle	19.2%	3.2%	2.7%	20.8%	49.5%	4.5%
2 cycles	20.9%	2.0%	1.0%	16.1%	54.4%	5.6%
3 cycles	19.0%	3.8%	0.8%	13.5%	55.6%	7.3%
3.5 cycles	18.8%	3.4%	0.6%	14.3%	56.1%	6.8%
6 cycles	9.3%	2.0%	1.0%	15.7%	62.8%	9.1%
11-mercaptoundecaneamide	46.4%	2.3%		6.9%	40.6%	3.9%
RO LE membrane				14.73%	74.23%	11.04%

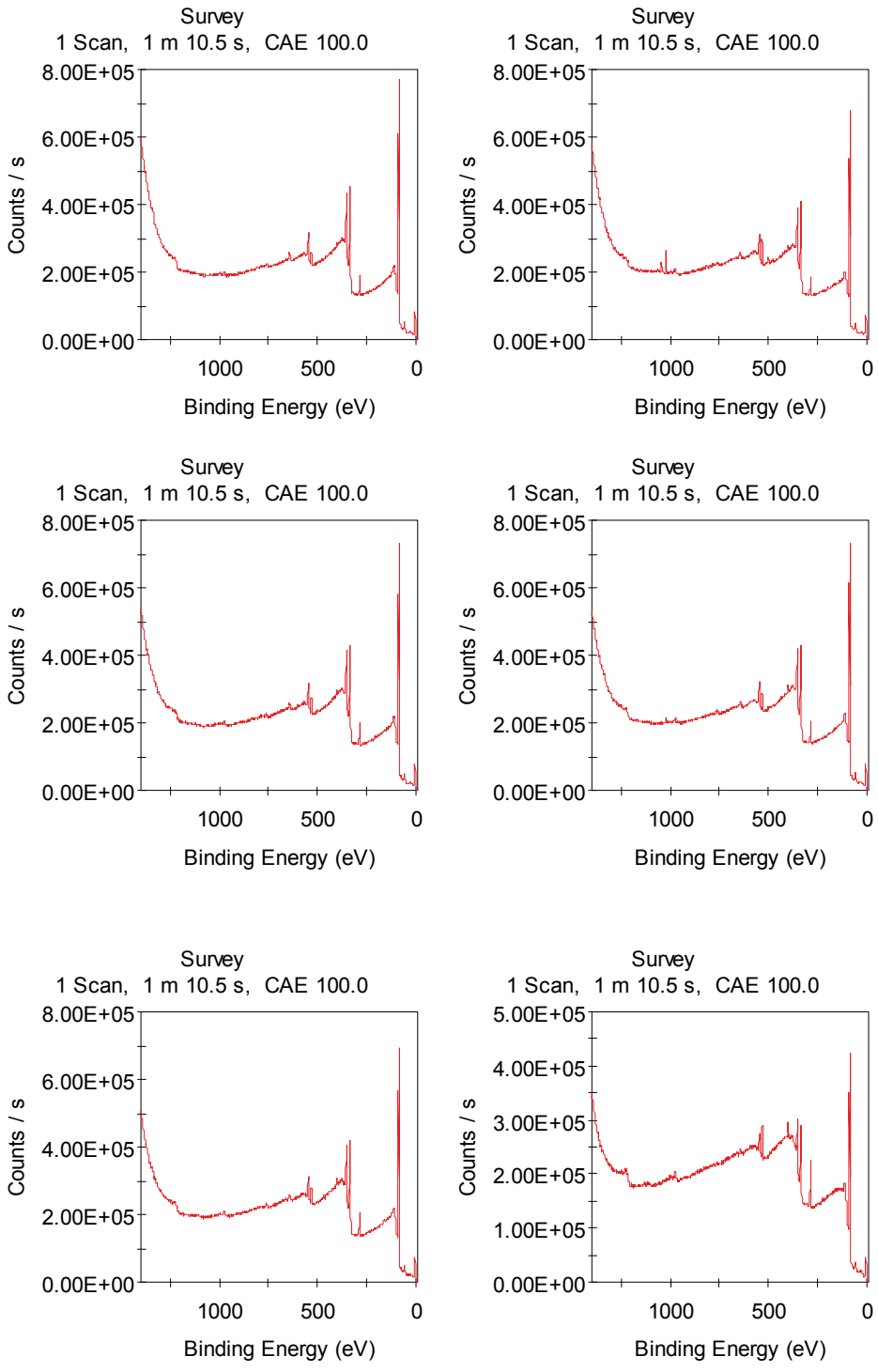

Figure S2: XPS general survey of cysteamine SAM (upper left), and of the various oligoamide-coated gold samples with 1 cycle preparation (upper right), 2 cycles (middle left), 3 cycles (middle right), 3.5 cycles (down left), and 6 cycles (down right).

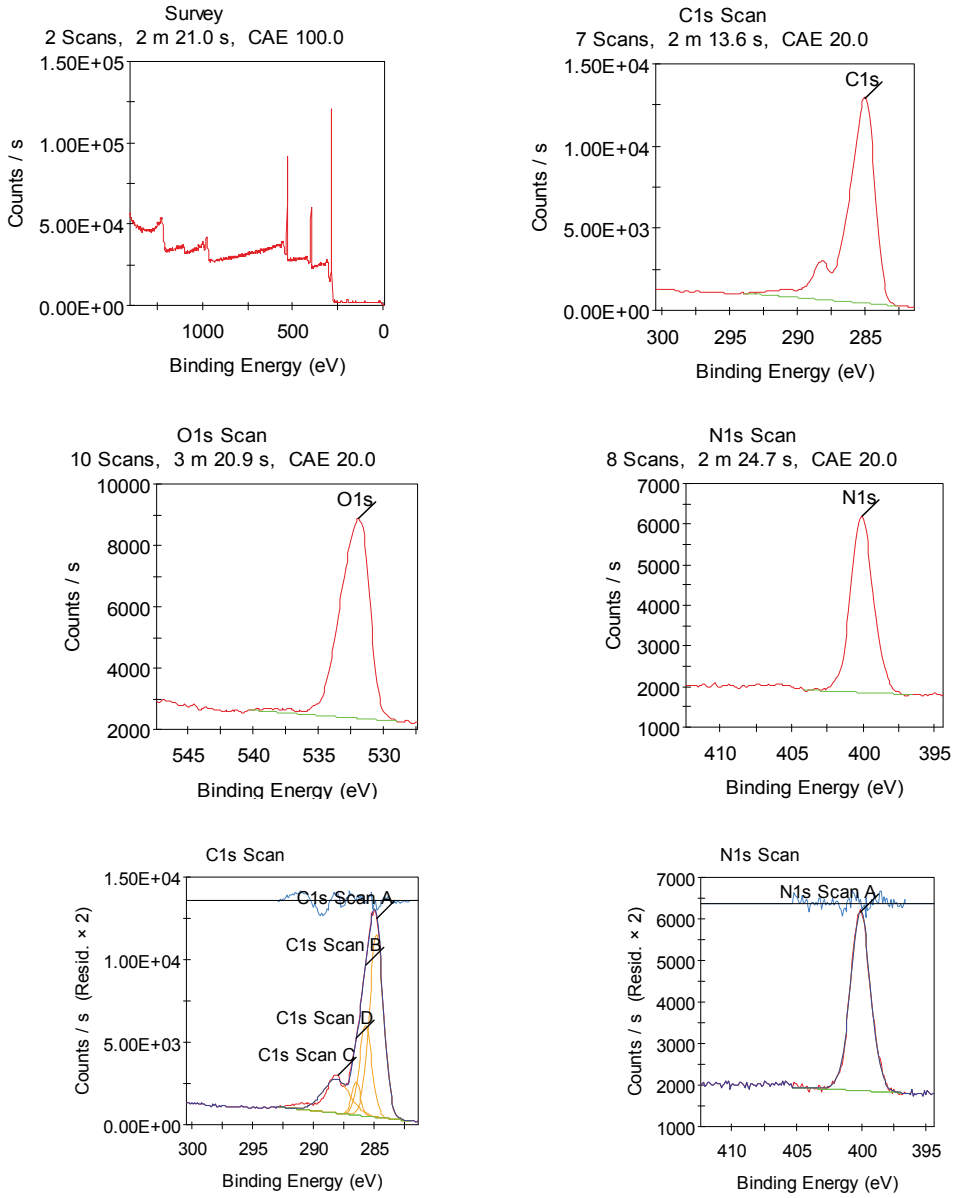

Figure S3: XPS general survey and specific peaks found of RO polyamide membrane type LE (FILMTEC, Dow Water Solutions).

Table S2: Surface elemental composition of oligoamide 6-cycle coated wafer in comparison to brackish water RO membrane type LE (by FILMTEC, Dow Water Solutions), measured by XPS.

	6 cycles oligoamide	RO membrane
N/C ratio	0.145	0.148
N/O ratio	0.576	0.75
O/C ratio	0.191	0.198
N	400.1 100%	400.1 100%
O	531.3 58.2%	531.5 41.2%
	532.1 17.1%	532.5 38.0%
	533.2 24.7%	533.5 20.8%
C	284.9 62.4%	284.8 53.0%
	285.9 18.3%	285.7 23.0%
		286.5 5.8%
	288.0 9.3%	288.0 18.2%
	288.7 10.0%	