

Supporting Information

Layer-by-Layer Assembly of Graphene Oxide Nanosheets on Polyamide Membranes for Durable Reverse Osmosis Applications

Wansuk Choi,^{†,‡} Jungkyu Choi,^{†,} Joona Bang,^{†,*} and Jung-Hyun Lee^{‡,*}*

[†]Department of Chemical and Biological Engineering, Korea University, 5-1 Anam-dong,
Seongbuk-gu, Seoul 136-713, Republic of Korea

[‡]Center for Materials Architecturing, Korea Institute of Science and Technology, 39-1
Hawolgok-dong, Seongbuk-gu, Seoul 136-791, Republic of Korea

* Address correspondence to jungkyu_choi@korea.ac.kr (J.C.), joona@korea.ac.kr (J.B.), and leejhy@kist.re.kr (J.-H.L.)

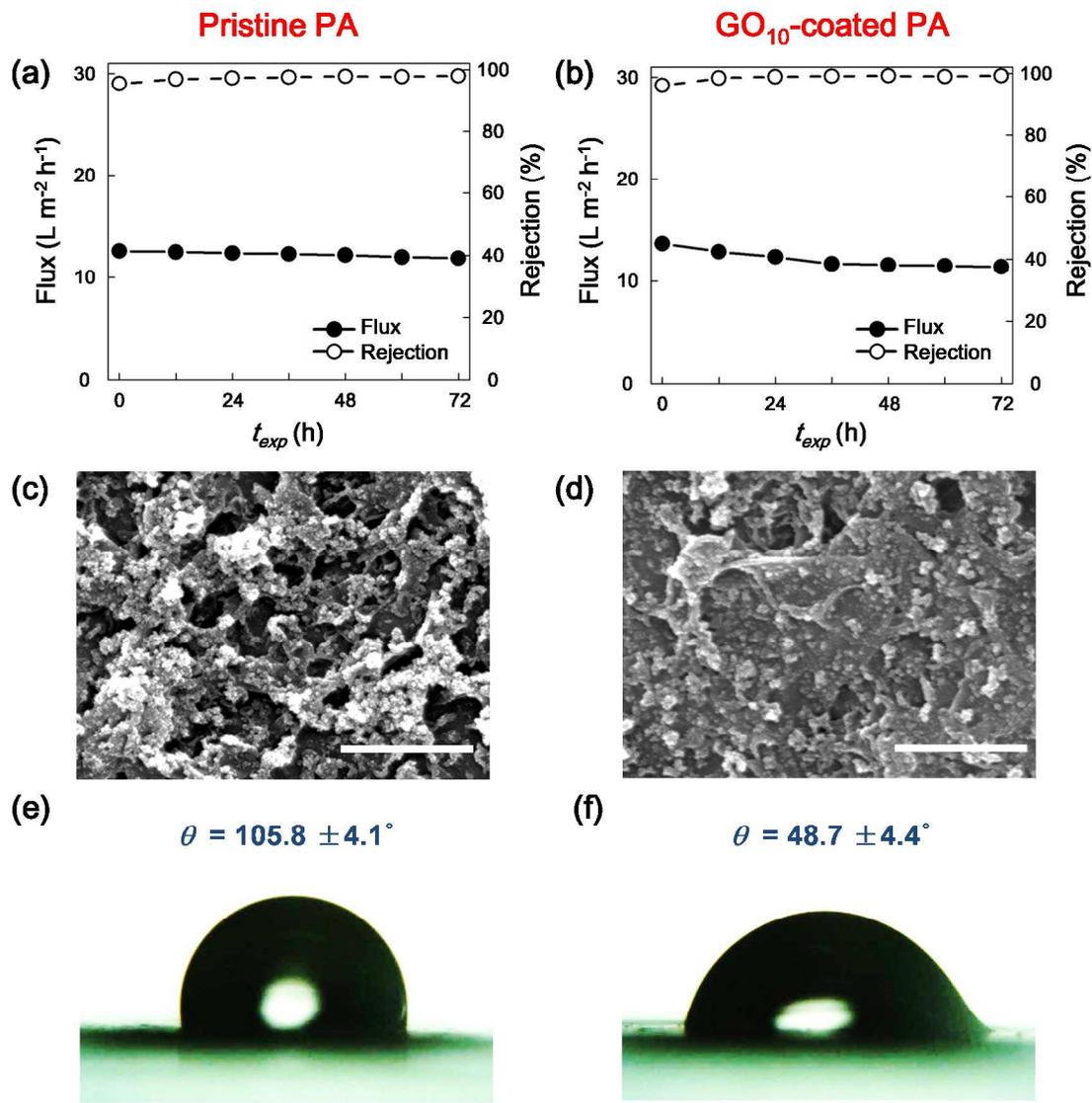


Figure S1. Long-term performance (water flux and NaCl rejection) data of (a) the pristine, uncoated polyamide (PA) and (b) the GO₁₀-coated PA membranes (Performance measurements were conducted using aqueous solution of 2,000 mg/L NaCl at pH 5.8 under an operating pressure of 15.5 bar for 72 h). Top-down SEM images (c and d, scale bar = 1 μm) and representative water contact angle images (e and f) of the pristine PA (left: c and e) and the GO₁₀-coated PA (right: d and f) membranes after performance test. Both the pristine PA and the GO₁₀-coated PA membranes exhibited no noticeable changes in performance over the entire

period of filtration time, indicating their long-term performance stability (Figures S1a and S1b). In addition, resistance of the GO layer to its detachment from the PA surface was verified by examining the surface morphology and evaluating water contact angle of the GO₁₀-coated PA membrane after performance test. SEM provides microscopic information of the surface morphology and it revealed that the GO layer remained intact without detachment after long-term filtration (Figure S1d). It should be noted that both the pristine PA and the GO₁₀-coated PA surfaces after performance test (Figures S1b and S1c) were slightly different from their counterparts before test (Figures 3a and 3b in the main text) due to the surface contamination resulting from inorganic scaling (by NaCl salt) and/or organic fouling (by unexpected organic debris present in the filtration apparatus) during the long-term filtration. Macroscopic evidence for the stability of the GO layer was also found from the measurement of water contact angle which was shown to be a good indicator of the presence of the GO layer as mentioned in the main text. The contact angle values after filtration test were higher than those before filtration test for both the pristine PA and the GO₁₀-coated PA membranes, which is attributed to the contaminants (residual salts and hydrophobic organic foulants) present on the membrane surfaces after the filtration test, as illustrated in SEM images (Figures S1c and S1d). Nevertheless, the GO₁₀-coated PA membrane still showed much lower water contact angle ($\theta = 48.7 \pm 4.4^\circ$) than that of the pristine PA membrane ($\theta = 105.8 \pm 4.1^\circ$), suggesting that the hydrophilic GO sheets are present on the PA surfaces.

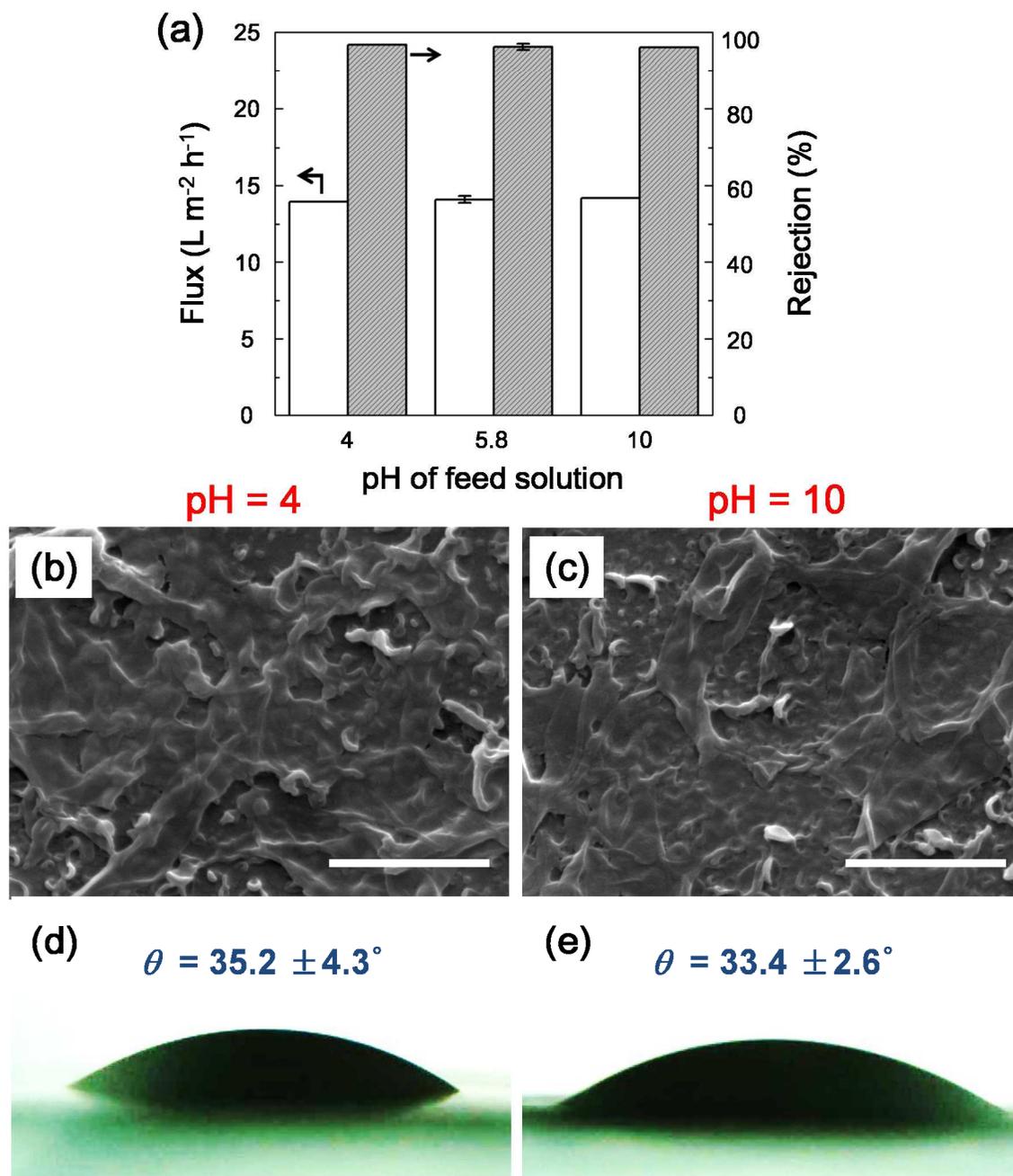


Figure S2. (a) Water flux and NaCl rejection of the GO₁₀-coated PA membranes as a function of the feed solution pHs (Performance measurements were conducted using aqueous solution of 2,000 mg/L NaCl under an operating pressure of 15.5 bar). Top-down SEM images (b and c, scale bar = 1 μm) and representative water contact angle images (d and e) of the GO₁₀-coated PA

membranes after performance test at pH = 4 (left: b and d) and 10 (right: c and e). No discernible difference in performance was observed over the range of the feed solution pHs (4 to 10) examined in this experiment (Figure S2a), illustrating the pH-stability of the GO₁₀-coated PA membranes. SEM surface images (Figures S2b and S2c) demonstrated that the GO layer firmly adhered to the PA surface after filtration test at pH = 4 and 10. In addition, considering that the water contact angle of membranes increases after performance test due to the surface contamination as mentioned above, the GO₁₀-coated PA membranes after filtration test at pH = 4 and 10 still exhibited quite low values of water contact angle ($\theta \approx 35^\circ$ and $\approx 33^\circ$, respectively), comparable to that before filtration experiment ($\theta \approx 26^\circ$ illustrated in the main text), which further suggests no delamination of the GO layer from the PA surface over the range of the operating pHs (4 to 10) together with the long-term filtration result at pH = 5.8 shown above.

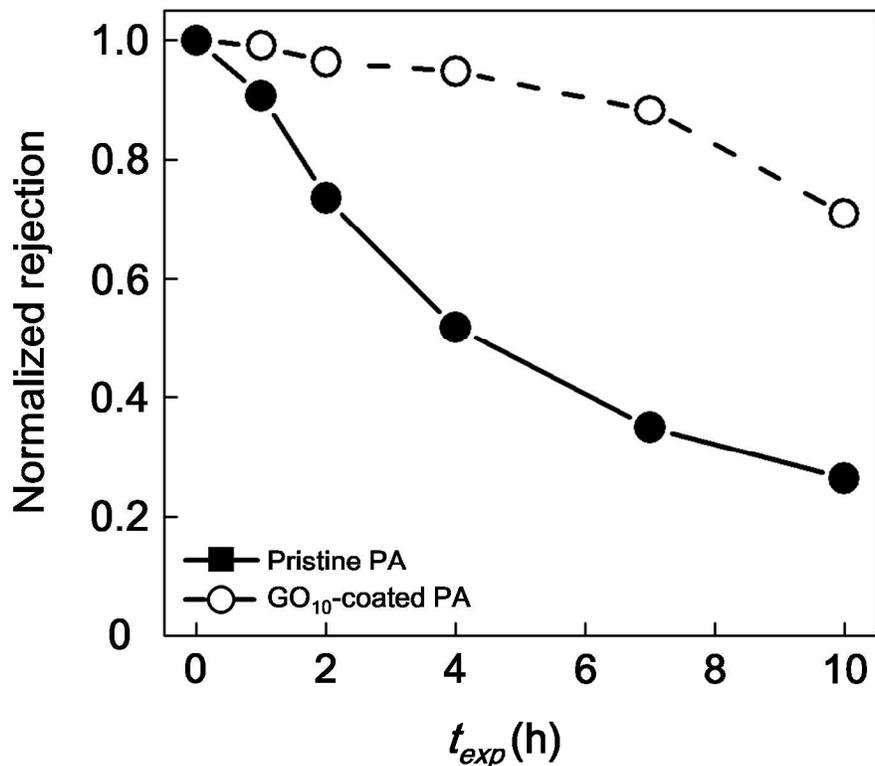


Figure S3. Changes in normalized NaCl rejection of the pristine, uncoated polyamide (PA) and the GO₁₀-coated PA membranes during the filtration with the feed solution containing 2,000 mg/L NaCl and 100 mg/L NaOCl (chlorine) as a function of filtration time (t_{exp}). The normalized values were obtained by dividing the measured values of the membranes after chlorination for a certain time by those before chlorination. This experiment simulates the realistic membrane exposure to the pressurized chlorine solution taking place during the actual cleaning process. The degree of chlorination can be compared between static exposure at 1 bar (soaking membranes into chlorine solution described in the main text) and pressurized exposure at 15.5 bar (exposing membranes to chlorine solution during filtration) in terms of the chlorine exposure level (the product of the NaOCl (chlorine) concentration and exposure time, ppm·h). Considering the unified term (ppm·h), pressurized chlorine exposure was shown to lead to higher degree of selectivity loss of membranes compared to the static exposure: Exposure of the pristine PA and

the GO₁₀-coated PA membranes to the pressurized chlorine solution (chlorine concentration = 100 mg/L) for 10 h (corresponding exposure level = 1,000 ppm·h) decreased salt rejection by ≈78% and ≈25%, respectively, which is remarkably higher degree of degradation than static exposure case where the rejection rates of ≈50% and ≈4% were estimated for the pristine PA and the GO₁₀-coated PA, respectively, even at higher chlorine exposure level (chlorine concentration of 6,000 mg/L for 1 h = 6,000 ppm·h) as illustrated in Figures 7b and 8b in the main manuscript. This result indicates that the pressurized chlorine exposure accelerates diffusion of active chlorine species into the PA selective layer and thus exacerbates the chlorine degradation in comparison with static exposure. Even in such a situation, the presence of the GO layer coating on the PA layer plays a predominant role in protecting the underlying PA layer and thus retarding chlorine-induced deterioration, as manifested in Figure S3 where the normalized rejection values of the GO₁₀-coated PA membrane maintained much higher than those of the pristine PA over the range of chlorine exposure time.