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Humidity-responsive Bilayer Actuators Comprised of Porous and Nonporous Poly(acrylic acid)/Poly(allylamine hydrochloride) Films

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Electronic Supplementary Information

Abstract Bilayer humidity-responsive actuators are generally composed of actuating and supporting layers of different materials with largely different wettability. Such kinds of bilayer actuators suffer from low adhesive force between the two layers during usage. This study demonstrates the preparation of humidity-responsive bilayer actuators that have the same materials in the actuating and supporting layers to avoid the adhesive issue. The bilayer actuators consist of a porous poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) layer and a nonporous PAA/PAH layer that are fabricated by exponentially layer-by-layer assembly method. At a high/low relative humidity (RH), the nonporous PAA/PAH layer can efficiently expand/shrink by absorbing/desorbing water while the volume expansion/shrinkage of the porous PAA/PAH layer in an environment with changed humidity is significantly suppressed by the micrometer-sized pores. The largely different expansion/shrinkage of the nonporous and porous PAA/PAH layers when subjected to humidity changes enables rapid and reversible rolling/unrolling motions of the bilayer actuator. The bilayer actuator shows a faster rolling speed and a larger bending curvature when subjected to a larger humidity increase.

Keywords Layer-by-layer assembly; Materials science; Porous films; Surface chemistry

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INTRODUCTION

Nature has developed numerous actuators capable of efficiently responding to various environmental changes such as light, temperature and humidity.^[1] These actuators in plants generate complicated shape deformations involving bending, folding, curling or twisting and accomplish vital tasks of plants such as the dispersal and self-burial of seeds. Inspired by these natural actuators, various artificial actuators have been developed to translate input energies generated by magnetic,^[2] electrical,^[3] photonic,^[4] thermal,^[5] pH^[6] and humidity^[7–10] changes into macroscopic two- or three-dimensional movements. As energy transducers, artificial actuators have important applications in the fabrication of sensors,^[11] switches,^[12] artificial muscles,^[9,13] micro-robotics,^[14,15] motors^[10,16] and power generators.^[7,10,17] Learning from natural actuators, artificial actuators usually adopt a bilayer structure in which two pieces of films with different responsive properties are interfacially bound to each other.^[14,15,17] The actuations of these bilayer actuators arise from different responsive behaviors of the intimately attached two layers under external stimuli. Alternatively,

artificial monolayer actuators made of homogeneous polymer composite films have also been developed, aiming to simplify the fabrication process of actuators.^[4,7,16] Under an external stimulus, monolayer actuator generates a bilayer-like structure consisting of responsive and non-responsive layers because the strength of the stimulus decays rapidly along the thickness direction of the actuator. For instance, Ikeda, Yu and coworkers have developed a number of light-driven actuators that can convert light energy directly into mechanical works such as contraction,^[18] bending,^[19] rotation,^[16] swimming^[20] and so forth. These actuators are cross-linked liquid-crystal polymer films containing photochromic molecules such as azobenzenes. When irradiated with UV light, the *trans* to *cis* photoisomerization of azobenzenes on the film surface leads to shrinkage of the surface layer, whereas the volume of the rest part of the film remains unchanged. Therefore, the asymmetric shrinkage of the film enables bending of the actuator toward light source.

Among the broad types of actuators, humidity-responsive actuators have attracted more attention of scientists because of the ubiquity of humidity changes in the natural environment. Humidity-responsive monolayer actuators can have good flexibility and mechanical robustness to convert humidity changes into electrical energy under an environment with humidity gradients.^[7,17] However, it is difficult to provide a humid environment with accurate and continuous humidity

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gradients. In contrast, precisely controlled humidity gradient is not necessary for the actuation of humidity-responsive bilayer actuators. Humidity-responsive bilayer actuators are usually comprised of a hydrophilic actuating layer and a hydrophobic supporting layer.^[15] Because of the different water-absorbing and swelling ability of the two layers, these bilayer actuators can generate mechanical motions in environments with either homogeneous or inhomogeneous humidity. Therefore, humidity-responsive bilayer actuators can accomplish complicated motions for use as artificial muscles,^[9] walking devices,^[21] and rotary engines.^[10] Despite these advantages, the adhesion between the interfaces of the bilayers poses a problem for long-term application of bilayer actuators because of the largely different wettability of the hydrophilic actuating layer and the hydrophobic supporting layer. Therefore, a new strategy for convenient fabrication of humidity-responsive bilayer actuators in which the two layers are made of the same materials without the concern of adhesive issue is highly required.

Polyelectrolyte films are ideal actuating layers in the fabrication of humidity-responsive actuators because of their high water absorbing/desorbing capacity.^[15,21,22] Besides the composition of polyelectrolytes, the conformation of polyelectrolyte chains in the actuating layers can also have a dramatic influence on the actuation behaviors of the humidity-responsive bilayer actuators. Layer-by-layer (LbL) assembly provides a powerful method for the fabrication of polyelectrolyte composite films with precisely controlled conformations of polyelectrolyte chains through alternate deposition of oppositely charged polyelectrolytes. Our previous work has demonstrated that LbL-assembled polyelectrolyte films are highly efficient in actuating humidity-responsive bilayer actuators.^[21,22] For example, we have recently reported a powerful humidity-responsive bilayer actuator comprising a water-absorbing layer of LbL-assembled poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) film and a water-inert layer of UV-cured Norland Optical Adhesive 63 (NOA-63).^[21] This bilayer actuator can drive an energetic walking device carrying a load 120 times heavier than the actuator to walk rapidly and steadily on a ratchet substrate by alternately changing the surrounding humidity. Taking advantages of bilayer actuators and LbL-assembled polyelectrolyte films, here in this work we demonstrate the fabrication of a unique humidity-responsive bilayer actuator comprising nonporous and porous PAA/PAH films that act as actuating and supporting layers, respectively. Because of the same composition of the porous and nonporous PAA/PAH layers, they have strong adhesion at the layer interface to avoid separation of the two layers. The nonporous PAA/PAH layer can absorb water to expand in an environment with increased humidity. Meanwhile, the pores of the porous PAA/PAH layer can provide free volume to suppress the expansion of the film after adsorption of water in increased RH. The largely different swelling ability of the porous and nonporous PAA/PAH layers, combined with their high flexibility and satisfactory mechanical robustness, enables reversible and fast rolling motions of the PAA/PAH bilayer actuators when environmental humidity is periodic-

ally altered.

EXPERIMENTAL

Materials

Poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in water, M_w ca. 1.0×10^5 to 2.0×10^5), PAA (M_w ca. 1800) and branched poly(ethylenimine) (bPEI, M_w ca. 7.5×10^5) were purchased from Sigma-Aldrich. PAH (M_w ca. 6.0×10^4) was purchased from Alfa Aesar. Hydrochloric acid and sodium hydroxide were analytical grade and were purchased from Beijing Chemical Reagents Company. All chemicals were used without further purification. Deionized water was used for all film fabrication. The pH values of the PAA and PAH dipping solutions for LbL-assembled films were adjusted with either $1 \text{ mol} \cdot \text{L}^{-1}$ HCl or $1 \text{ mol} \cdot \text{L}^{-1}$ NaOH.

LbL Assembly of Nonporous and Porous PAA/PAH Films

The nonporous and porous (PAA/PAH)* n films are denoted as NP-(PAA/PAH)* n and P-(PAA/PAH)* n films, respectively (where n refers to the number of film deposition cycles; a half cycle means PAA is the outmost layer). The freshly cleaned silicon or quartz substrate was first immersed in an aqueous PDDA solution ($1 \text{ mg} \cdot \text{mL}^{-1}$, pH 5.5) for 20 min and then rinsed with water for 1 min to obtain a positively charged surface. The LbL assembly of PAA/PAH films on PDDA-modified substrate was conducted automatically by a programmable dipping machine at room temperature. The PDDA-modified substrate was immersed in an aqueous PAA solution ($1 \text{ mg} \cdot \text{mL}^{-1}$, pH 3.5) for 15 min and then rinsed in deionized water baths three times with 1 min for each time. The substrate was then immersed in an aqueous PAH solution ($1 \text{ mg} \cdot \text{mL}^{-1}$, pH 7.5) for another 15 min and rinsed in deionized water baths three times with 1 min for each time. The immersion in PAA and PAH dipping solutions and the water rinsing step were repeated in a cyclic fashion to obtain (PAA/PAH)* n films with a desired number of deposition cycles. No drying step was used in the deposition procedure unless it was in the last layer. The as-prepared PAA/PAH films were nonporous. To obtain porous PAA/PAH films, the as-prepared PAA/PAH films were first immersed in an acidic aqueous solution (pH 3.0) for 30 min and then transferred immediately into deionized water (pH 6.5) for 2 min. The porous and nonporous PAA/PAH films were thermally cross-linked by heating at 180°C or 150°C in a vacuum oven.

Preparation of Free-standing P-(PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 Films

The fabrication of free-standing P-(PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 film is schematically shown in Fig. 1. For simplicity, the P-(PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 films are denoted as P/NP films. The process includes the LbL assembly of (PAA/PAH)*20.5/cross-linked-(PAA/PAH)*30.5 film on the substrate, the formation of pores in the (PAA/PAH)*20.5 layer and the exfoliation of the whole film from the underlying substrate. As-prepared (PAA/PAH)*30.5 film was heated at 150°C for 1 h to produce thermally cross-linked NP-(PAA/PAH)*30.5 film. The

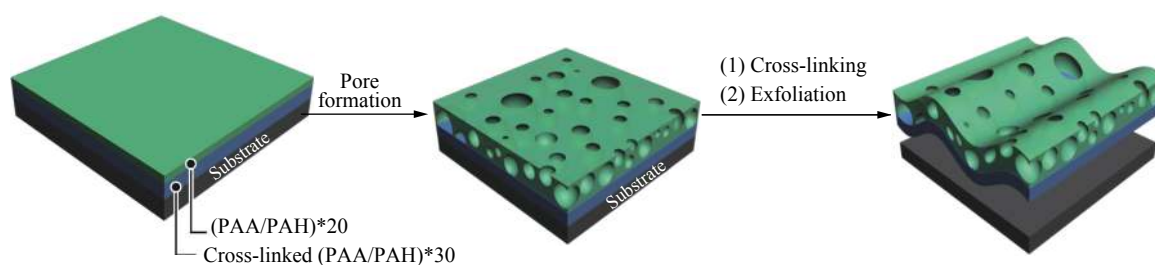


Fig. 1 Schematic illustration of the fabrication of P/NP films and their release from substrates to produce free-standing films

cross-linked NP-(PAA/PAH)*30.5 film was then immersed in an aqueous bPEI solution ($1 \text{ mg} \cdot \text{mL}^{-1}$, pH 7.5) for 15 min to deposit a PEI layer. Next, P-(PAA/PAH)*20.5 film was fabricated on top of the bPEI-modified NP-(PAA/PAH)*30.5 film by LbL assembly of (PAA/PAH)*20.5 film followed with pore formation steps. Finally, the P/NP film was cross-linked by heating at 180°C for 2 h to further enhance its mechanical robustness. Free-standing P/NP film was obtained by immersing the film into an acidic aqueous solution (pH 2.3) for 10 min. To facilitate the exfoliation of the P/NP film from the underlying substrate, the film on the edges of the substrate was cut off with a knife.^[22]

Film Characterization

Film thickness was measured using a Dektak 150 profilometer with a 3 mg stylus force. Scanning electron microscopy (SEM) images were obtained on an XL30 ESEM FEG scanning electron microscope. Atomic force micro-

scopy (AFM) images were taken on a Nanoscope IIIa AFM Multimode instrument under tapping mode. Quartz crystal microbalance (QCM) measurements were taken with a KSV QCM-Z500 instrument using quartz resonator with both sides coated with Ag ($F_0 = 9 \text{ MHz}$). Digital camera images and videos were captured by a Sony DCR-SR62E camera.

RESULTS AND DISCUSSION

The LbL assembly of (PAA/PAH)* n films was conducted on PDDA-modified silicon substrates. The driving forces for the fabrication of the (PAA/PAH)* n film are the electrostatic and hydrogen-bonding interactions between carboxylate groups of PAA and amine groups of PAH. Figs. 2(a) and 2(b) show the thickness of the (PAA/PAH)* n films as a function of the number of film deposition cycles. In the initial 10 deposition cycles, the film thickness exhibits a typically exponential growth behavior.^[21–23] After 10 depo-

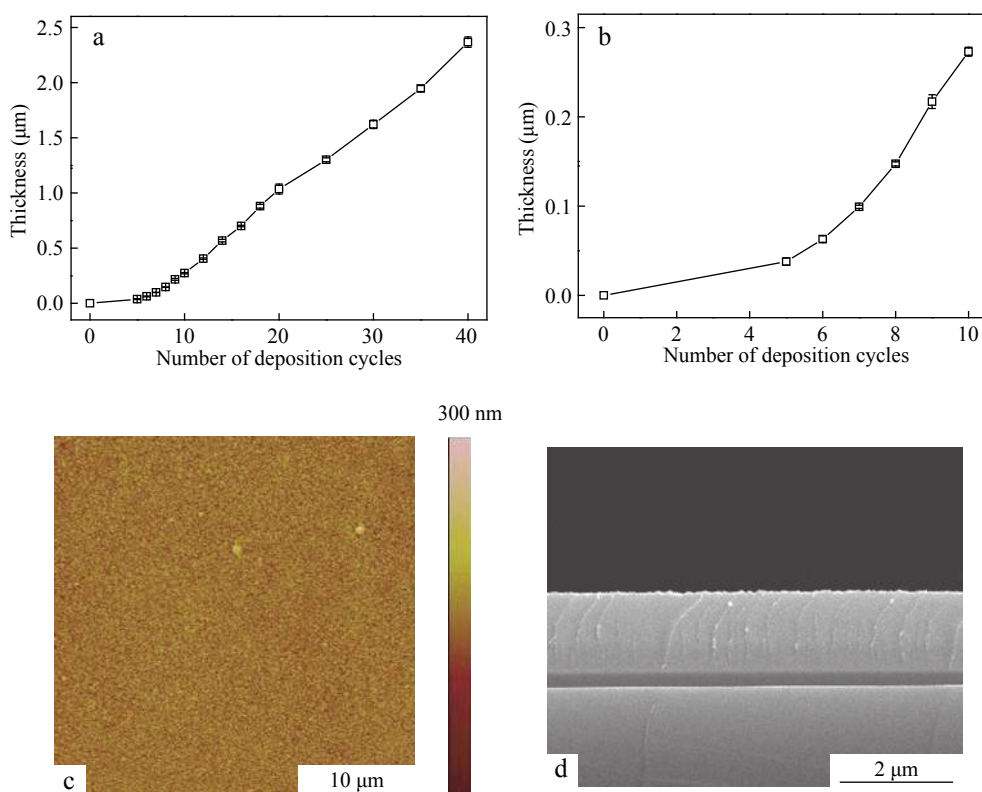


Fig. 2 (a, b) Thickness of (PAA/PAH)* n films as a function of the number of film deposition cycles drawn with different abscissa scales; (c) AFM and (d) cross-sectional SEM images of a cross-linked NP-(PAA/PAH)*30.5 film

sition cycles, the thickness of the PAA/PAH films increases almost linearly, with an average increment of ~ 70 nm for one cycle of PAA/PAH film. The (PAA/PAH)*30.5 films have an average thickness of ~ 1.7 μm . Based on our previous reports, the exponential LbL assembly of PAA and PAH is ascribed to the “in-and-out” diffusion of PAA and PAH chains during the film deposition process.^[21–23] Taking PAA as an example, an excessive amount of PAA can diffuse into the PAA/PAH film when the film is immersed into aqueous PAA dipping solution. During the process of subsequent immersion of the PAA/PAH films into aqueous PAH dipping solution, the deposited PAA can diffuse out of the film to complex an excessive amount of PAH at the film-solution interface. The “in-and-out” diffusion of PAA and PAH leads to more amount of PAA and PAH deposition in the current deposition cycle than in the previous one. As the number of film deposition cycles increases, the amount of the diffused PAA and PAH gradually reaches constant and the (PAA/PAH)* n film undergoes a linear deposition process.^[23] The exponential LbL assembly process enables the fabrication of (PAA/PAH)* n films with highly interpenetrated PAA and PAH layers. The as-prepared (PAA/PAH)*30.5 films were heated at 150 $^{\circ}\text{C}$ for 1 h to produce slightly cross-linked (PAA/PAH)*30.5 films. The appearance of the absorbance peak at ~ 1670 cm^{-1} in the Fourier transform infrared (FTIR) spectrum of the heated (PAA/PAH)*30.5 film confirms the formation of amide bonds between carboxylate and amine groups. AFM image in Fig. 2(c) indicates that the cross-linked (PAA/PAH)*30.5 films have a smooth and compact surface with a root-mean-square (RMS) roughness of (16.3 ± 0.2) nm in a measured area of 40 $\mu\text{m} \times 40$ μm . Cross-sectional SEM image in Fig. 2(d) shows that the cross-linked NP-(PAA/PAH)*30.5 film has a constant thickness of (1.41 ± 0.02) μm .

The cross-linked NP-(PAA/PAH)*30.5 film was first de-

posited with a layer of bPEI, on which LbL assembly of (PAA/PAH)*20.5 film was conducted to fabricate the (PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 film. As shown in Fig. 3(a), the (PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 film has a smooth surface with a RMS roughness of (12.7 ± 0.4) nm in a measured area of 40 $\mu\text{m} \times 40$ μm . Cross-sectional SEM image in Fig. 3(b) shows the interface between the cross-linked NP-(PAA/PAH)*30.5 film and the as-prepared (PAA/PAH)*20.5 film. The thicknesses of the (PAA/PAH)*20.5 film is (1.22 ± 0.04) μm . The (PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 film was immersed in an acidic aqueous solution (pH 3.0) to induce the formation of pores in the (PAA/PAH)*20.5 film. Top view SEM image of the P/NP film in Fig. 3(c) shows that the pore size is in the range of 1.2 μm to 5.5 μm . The pores are densely arranged and most of them are closed with a thin PAA/PAH film. The cross-sectional SEM image of P/NP films in Fig. 3(d) reveals that the porous layer is in intimate contact with the underlying nonporous layer. The total thickness of the film is (4.20 ± 0.17) μm , in which the top porous layer is (2.78 ± 0.18) μm . Immersion of the (PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 film in acidic aqueous solution can partially break the electrostatic and hydrogen-bonding interactions in the non-cross-linked (PAA/PAH)*20.5 layer by protonating the carboxylate groups in PAA and amine groups in PAH. This process results in the large-scale phase separation of PAA and PAH, inducing the formation of micrometer-sized pores in (PAA/PAH)*20.5 film.^[23] The large-scale phase separation of PAA and PAH arises from the high interpenetration of PAA and PAH chains, which significantly enhances the mobility of PAA and PAH chains in the exponentially grown PAA/PAH film during phase separation process.^[23] The immersion of the porous film in water of pH 6.5 can stabilize the pores by deprotonating the carboxylic acid and the protonated amine groups to re-establish electrostatic and hydro-

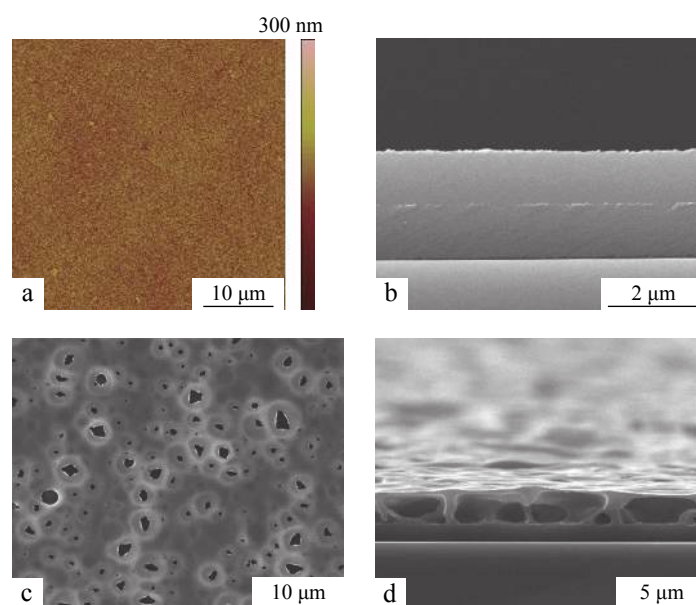


Fig. 3 (a) AFM and (b) cross-sectional SEM images of a (PAA/PAH)*20.5/NP-(PAA/PAH)*30.5 film; (c) top-view and (d) cross-sectional SEM images of a P/NP film

gen-bonding interactions in the porous (PAA/PAH)*20.5 film.^[23] The P/NP films were thermally cross-linked at 180 °C for 2 h to further improve their stability. Large area free-standing P/NP film can be obtained by immersing the cross-linked film into an aqueous solution with a pH of 2.3.^[22] The H⁺ ions in aqueous solution can protonate PAA and break the electrostatic interaction between PDDA-modified substrate and the bottom PAA layer, exfoliating the P/NP film from the underlying substrate.

The free-standing P/NP film was cut into 7.5 mm × 13.0 mm strips to produce actuators. The actuator is fixed on a solid plate on one end with the P-(PAA/PAH)*20.5 layer facing upward (Fig. 4). The humidity response of the actuator is investigated by changing the environmental relative humidity (RH) from 35% to 70% (Movie 1, in electronic supplementary information, ESI). The actuator is nearly flat at 35% RH. When the actuator is moved to an environment of 70% RH, it rolls up quickly in 31 s with the NP-(PAA/PAH)*30.5 layer facing outward (Fig. 4a). Moving the rolled P/NP film back to the environment of 35% RH, it unrolls to its initial configuration within 12 s (Fig. 4b). The rolling and unrolling processes are reversible and reproducible when RH is periodically altered between 35% and 70%. The rolling/unrolling movements of the actuator demonstrate that porous and nonporous PAA/PAH layers in the actuator can respond differently in an environment with a changed humidity.

To clarify the mechanism of rolling/unrolling motions of the actuators, the water absorption abilities of the nonporous and porous PAA/PAH films were characterized by quartz crystal microbalance (QCM) measurements.^[22] The mass percentages (ΔM) of water absorbed by the NP-(PAA/PAH)*7 and P-(PAA/PAH)*7 films when transferred from 0% RH to

100% RH were calculated to be $(15.4 \pm 0.4)\%$ and $(10.7 \pm 0.3)\%$, respectively. Although the NP-(PAA/PAH)*7 layer can absorb more water than the P-(PAA/PAH)*7 layer when environmental RH increases, the ~4.7% difference in water absorption capability is insufficient to induce such a large and rapid rolling/unrolling motion of the bilayer actuators according to our previous studies.^[21,22] We believed that the significant structural difference between the nonporous and the porous PAA/PAH layer as well as their different water absorption capability leads to the rapid motions of the P/NP actuator when subjected to humidity changes. The volume of the nonporous PAA/PAH film can efficiently expand by absorbing water in an environment with increased RH. During the film expansion process, the PAA and PAH chains change from coiled conformations to more extended conformations. For the porous PAA/PAH film, the micrometer-sized pores can provide large free volume to greatly suppress the expansion of the film caused by the absorbed water in increased RH. As depicted in Fig. 4(c), the asymmetric expansion of the nonporous and porous layer in an environment with an increased humidity can induce a strong interfacial stress, which enables rapid rolling of the P/NP actuator. When the RH decreases, the nonporous PAA/PAH layer shrink due to water desorption, leading to unrolling of the actuator to its original state.

The rolling/unrolling speed of the P/NP actuator relies on the RH changes (Fig. 5). The actuator needs 3 s to start rolling when moved from 35% RH to 55% RH (Movie 2, in ESI). When transferred from 35% RH into an environment with 70% and 90% RH, the actuator rolls immediately (within 1 s) (Movies 1 and 3, in ESI). The time required for full rolling of actuator when transferred from 35% RH into the

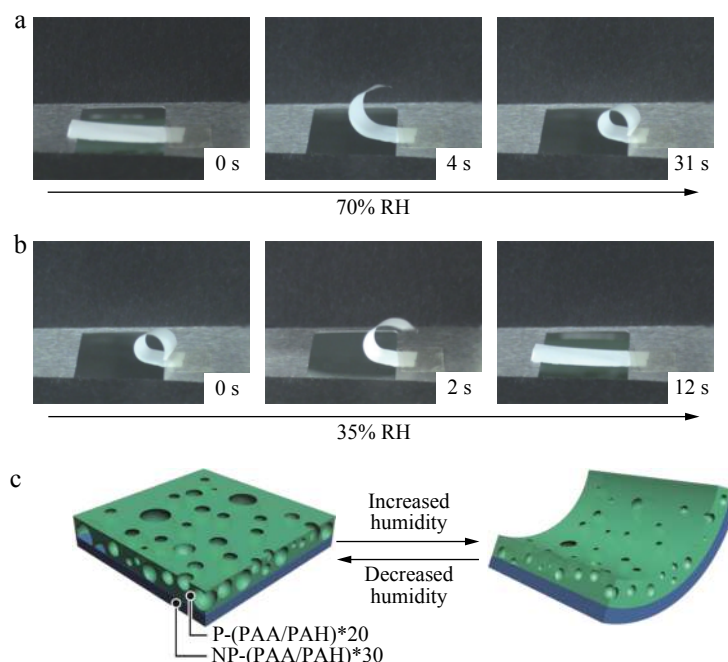


Fig. 4 (a, b) Time profiles of rolling and unrolling motion of a P/NP actuator (7.5 mm × 13 mm) by changing the RH (a) from 35% to 70% and (b) from 70% to 35%; (c) schematic illustration of the rolling/unrolling actuation of a P/NP actuator toward humidity changes

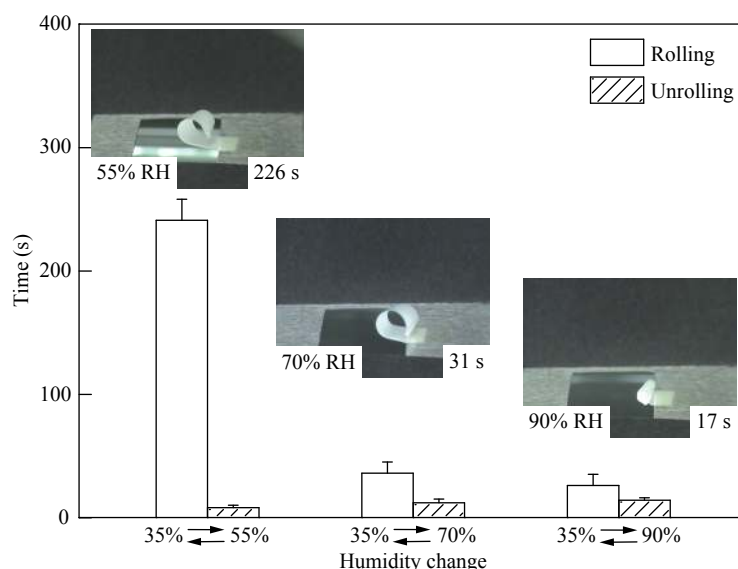


Fig. 5 The rolling/unrolling time of a P/NP actuator under different humidity changes (The insets show the photographs of the final states of the rolled actuator at different RH.)

environment with 55%, 70% and 90% RHs is ~226, ~31 and ~17 s, respectively. The actuator shows a shorter startup time, a faster rolling speed and a larger bending curvature under a larger humidity increase. It takes 9, 12 and 13 s for the rolled actuator to return to its original state when transferred from 55% RH, 70% RH and 90% RH back to 35% RH, respectively, meaning that the unrolling speed slightly decreases with humidity increase. This is because the actuator needs a longer time to desorb water to its original state when it absorbs more water. From Fig. 5, it is clear that the unrolling time of the actuator is much shorter than the rolling time. The extended PAA and PAH chains in water-absorbed PAA/PAH film tend to relax to their entropically favored coiled conformational state when environmental RH decreases, explaining why the unrolling process is faster than the rolling process.

CONCLUSIONS

We presented a novel method for the fabrication of highly efficient humidity-responsive bilayer actuators in which the actuating and supporting layers are composed of the same polyelectrolyte films. The humidity-responsive bilayer actuator comprises a nonporous PAA/PAH film as the actuating layer and a porous PAA/PAH film as the supporting layer. The nonporous PAA/PAH layer can absorb water to expand its volume in an environment with increased RH. Although the porous layer can also absorb water under increased RH, the high density of micrometer-sized pores can provide sufficient free volume to suppress the volume change of the porous layer. The expansion/shrinkage difference of the nonporous and porous PAA/PAH layers enables rapid and reversible rolling/unrolling motions of the bilayer actuators. The integration of films with the same materials and different structures provides a new way to fabricate highly efficient humidity-responsive bilayer actuators with enhanced adhe-

sion between the actuating and supporting layers. We believe that this design strategy can also be extended for the fabrication of other kinds of bilayer actuators that respond to various stimuli such as light, heat, electricity and so forth.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2162-3>.

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