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Humido- and Thermo-Responsive Free-Standing Films Mimicking the Petals of the Morning Glory Flower

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The mimic of petals of the morning glory flower can produce novel humido- and thermo-responsive membranes. In this work, humido- and thermo-responsive film has been fabricated by vacuum deposition of a nanoscale-thick aluminum layer on top of the thermally cross-linked poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) free-standing film. The bilayer Al/(PAA/PAH) film can undergo bending/unbending movements when the environmental humidity and/or temperature changes, which mimics the petals of morning glory flowers. The bending/unbending movement of the bilayer films is caused by the large difference in response of the aluminum layer and the PAA/PAH polymeric film toward humidity and temperature. The present study provides a simple and flexible way to prepare novel humido- and thermo-responsive film materials.

Introduction

Materials capable of stimulus-responsive movements have attracted much attention because of their ability to change their volume and shapes in response to external stimulus.[1−5] The movements include two-dimensional expansion/contraction and three-dimensional bending/unbending.[6] Compared with expansion and contraction, stimulus-responsive materials showing reversible bending/unbending movements under the external stimuli such as changes in temperature,[7,8] humidity,[9,10] solvent composition,[8] pH,[10] light,[3,5,11,12] electric field,[13,14] and magnetic field,[15,16] hold great promises in applications as actuators, cantilever sensors, transducers, micropumps, artificial muscles, and switching devices. Mother Nature has created numerous responsive matters, beneficial from the long-term evolution. For instance, the petal of the morning glory flower is a kind of excellent humid and thermal sensitive membrane. Just like the name implies, morning glory flowers are funnel-shaped and open in the morning. The big and thin petals of the morning glory flower can absorb sufficient water under a moderate low temperature which expands the petals, leading to the flower blooming. With the increase of temperature, the moisture decreases. Water in the flower vaporizes, and the petals curl quickly, leading to the senescence of the flowers around noon. Mimicking the petals of the morning glory flower will produce novel humido- and thermo-responsive membranes.

Free-standing films are of great interest for use in microelectromechanical devices in the form of sensors or actuators that endure repeated usage.[17,18] Among many kinds of free-standing films, LbL assembled free-standing films have captured more interest of scientists because of the flexibility of the LbL assembly technique in precisely tailoring film structures and composition.[18−21] The convenience in fine tailoring the composition and structure of LbL assembled films[22−24] will be of great help in fabricating free-standing films with fast and reversible response and further decorating the free-standing films for target response. However, the responsive free-standing LbL assembled films capable of reversible bending/unbending movements are seldom seen. In our previous study, we developed an ion-

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triggered method for the preparation of free-standing LbL assembled films.[25] The release of the LbL assembled films from the substrate was achieved by breaking the interaction of the first layer of the films with the underlying substrate while keeping the integrity of the resultant films. Herein, we report the preparation of humido- and thermo-responsive bilayer coatings by vacuum deposition of aluminum with nanometer thickness on a cross-linked poly(acrylic acid) (PAA)/poly(allylamine hydrochloride) (PAH) free-standing film. This kind of metal/polymer bilayer Al/(PAA/PAH)**n* film mimics the behavior of petals of the morning glory flower under the changes of environmental humidity and temperature.

Experimental Section

Materials. Poly(acrylic acid) (PAA, Mw ca. 2000), poly(allylamine hydrochloride) (PAH, Mw ca. 70 000), and poly(diallyldimethylammonium chloride) (PDDA, 20 wt %, Mw ca. 100 000−200 000) were purchased from Sigma-Aldrich. All chemicals were used without further purification. The concentration of polymer solutions used for all experiments was 1 mg mL^{-1} made from 18 MΩ Millipore water, and further pH was adjusted by either 1 M HCl or 1 M NaOH.

PAA/PAH Film Preparation. The LbL deposition of PAA/PAH multilayer films was conducted automatically by a programmable dipping machine (Dipping Robot DR-3, Riegler & Kirstein GmbH) at room temperature.[25−27] The freshly cleaned silicon wafer was immersed in a PDDA aqueous solution (pH 5.9) for 20 min to obtain a cationic ammonium-terminated surface and was ready for PAA/PAH multilayer deposition. Next, the substrate was immersed into an aqueous PAA solution (pH 3.5) for 20 min to obtain a layer of PAA film. The substrate was then rinsed in four deionized water baths (pH ~ 6.5, without pH adjustment) for 1 min each before the next layer deposition. Next, the substrate was immersed into an aqueous PAH solution (pH 7.5) for 20 min to obtain a layer of PAH film. After water rinsing as in the case of PAA layer deposition, the substrate was immersed into an aqueous PAA solution to deposit another layer of PAA. The adsorption and rinsing steps were repeated until the desired number of bilayers was obtained. No drying step was used in the film deposition procedure. The thermal cross-linking of PAA/PAH was conducted by heating the film at 180 °C for 2 or 7 h in a vacuum oven.

Aluminum Deposition. The aluminum layer was thermally evaporated at a rate of 10 Å/s under the pressure of around 3.5×10^{-4} Pa by a KY-400 type vacuum evaporator (Institute of Shenyang Keyou Vacuum Evaporation Technology).

Characterization. Scanning electron microscopy (SEM) images were obtained on a XL30 ESEM FEG scanning electron microscope. Atomic force microscopy (AFM) images were taken on a Nanoscope IIIa atomic force microscope (Digital Instruments, Santa Barbara, CA). Digital camera images and videos were captured by using Sony digital video camera recorder (DCR-SR62E). Stress−strain curves of the thermally cross-linked free-standing PAA/PAH films were measured with a mechanical strength microtest (Deben, U.K.).

Results and Discussion

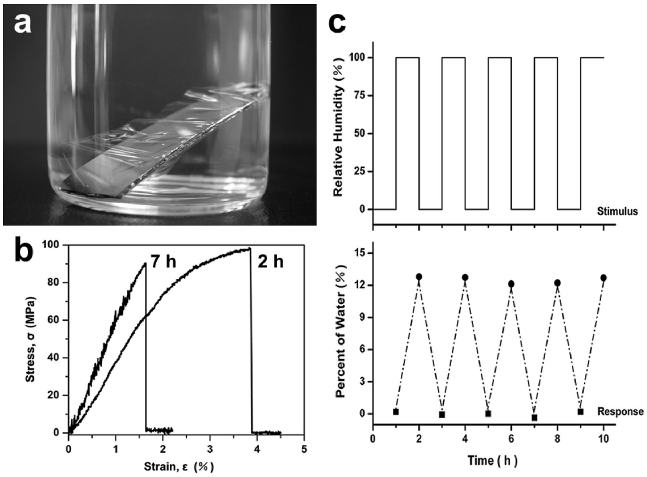

Figure 1. (a) Photograph of a thermally cross-linked (PAA/PAH)*30 multilayer film (1.0 × 3.0 cm^2) deposited on a silicon wafer after being exfoliated in water with a pH of 2. (b) Typical stress−strain curves for thermally cross-linked (PAA/PAH)*30 free-standing films heated at 180 °C for 2 and 7 h. (c) Percentage of water adsroption in a thermally cross-linked (PAA/PAH)*7 film when the relative humidity changed from 0% RH to 100% RH.

Thermally cross-linked PAA/PAH free-standing films were obtained by an ion-triggered exfoliation method.[25] To facilitate the exfoliation of the film, the edges of the sample were scratched or cut off with a knife. As indicated in Figure 1a, when a thermally cross-linked (PAA/PAH)*30 film (1.0 × 3.0 cm^2) deposited on silicon wafer was immersed in an aqueous solution with a pH of 2.0 for 5 min, a defect-free PAA/PAH free-standing film with large areas was released from the substrate by slightly shaking the substrate in the exfoliation solution. The main concern about the free-standing PAA/PAH film for use as a robust film material is its mechanical property. The thermally cross-linked PAA/PAH free-standing films exhibit excellent mechanical property, as indicated in the typical stress (σ) versus strain (ε) curves obtained for the cross-linked (PAA/PAH)*30 free-standing films in Figure 1b. The ultimate tensile strength (σ_u) of the cross-linked (PAA/PAH)*30 film heated for 2 h reaches 96 ± 3 MPa, which exceeds the value for some typical strong industrial plastics (the value of which is 20−66 MPa).[28] Its Young's modulus (E) is 4.3 ± 0.1 GPa. The initial part (0−0.5% strain) of the stretching curve is a short elastic deformation region where the stretching leads to bond bending and stretching of polymer chains.[19] On further stretching, the inelastic deformation region takes up the main part of the stretching curve. The stretching curve is nonlinear in the inelastic deformation region, which elucidates that the thermally cross-linked PAA/PAH film is tough. Its toughness is based on a successive breaking of polymer intra- and interchain loops with different characteristic energy, which formed from different polymer segments by van der Waals, hydrogen bonds, and ionic interactions. Here, the thermal cross-linking resulted in covalent amide bonds between PAA and PAH,[29,30] sharply enhancing the mechanical property of the PAA/PAH free-standing films. The ultimate strain (ε)

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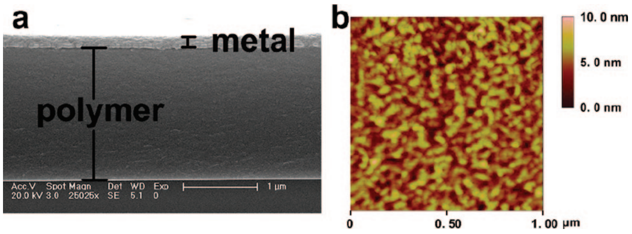

Figure 2. (a) Cross-sectional SEM image of a bilayer film obtained by evaporating a layer of aluminum on top of a thermally cross-linked (PAA/PAH)*30 free-standing film. (b) AFM image of the evaporated aluminum layer.

of (PAA/PAH)*30 films thermally cross-linked at 180 °C for 2 h is 3.3 ± 0.5%, and their toughness is 1.9 ± 0.5 MJ m^{-3}. These data show that the thermally cross-linked PAA/PAH free-standing films are strong and tough enough to be used as film materials. Furthermore, our study showed that an excessive long time of thermal cross-linking decreased the mechanical property of the free-standing PAA/PAH films. For instance, the (PAA/PAH)*30 film after thermal cross-linking at 180 °C for 7 h has a tensile strength of 94 ± 8 MPa, which almost maintains the same as that of PAA/PAH free-standing films thermally cross-linked for 2 h. But its ultimate strain declines to 1.6 ± 0.1% and toughness to 0.9 ± 0.3 MJ m^{-3}. Its Young's modulus increased to be 5.0 ± 0.6 GPa. Therefore, the heavily cross-linked PAA/PAH free-standing films are strong but not tough enough. In the following experiments, all of the PAA/PAH free-standing films were thermally cross-linked at 180 °C for 2 h.

As indicated in Figure 1c, thermally cross-linked PAA/PAH multilayer films are water-absorbable. A (PAA/PAH)*7 film deposited on a silver-covered quartz crystal microbalance resonator ($F_0 = 9$ MHz) was thermally cross-linked at 180 °C for 2 h and was alternatively equilibrated for 1 h in an environment with a relative humidity (RH) of 0% and 100%. The frequency shifts caused by the film deposition and water adsorption were recorded. The mass percentage (ΔM) of water adsorbed by the film when transferred from an environment with 0% RH to 100% RH can be calculated by the equation

$$\Delta M\ (\%) = \frac{\Delta F_{100\%} - \Delta F_{0\%}}{\Delta F_{0\%}} \times 100 \qquad (1)$$

Herein, $\Delta F_{100\%}$ and $\Delta F_{0\%}$ are the frequency decreases of the QCM resonator with the (PAA/PAH)*7 film at a relative humidity of 100% and 0% compared with the bare one, respectively. ΔM was calculated to be 12.5 ± 0.3% of the film mass at 0% RH. The absorbed water can swell the PAA/PAH films.[31,32]

The bilayer metal/polymer film was prepared by vacuum deposition of aluminum with nanometer thickness on a thermally cross-linked PAA/PAH free-standing film. The cross-sectional scanning electron microscopy (SEM) image of the bilayer film allows direct measurement of the film thickness, as presented in Figure 2a. The as-prepared (PAA/PAH)*30 film has a thickness of ~2.74 μm.[25] The large film thickness originates from the exponential deposition behavior of PAA/PAH films because of the diffusion "in" and "out" of PAA and PAH chains during multilayer film fabrication.[26] The thickness of a thermally cross-linked (PAA/PAH)*30 polymer film is 1.79 ± 0.01 μm. Obviously, thermal cross-linking leads to shrinkage of the film. The aluminum layer, which has intimate contact with the underneath PAA/PAH film, has a constant thickness of 157 ± 6 nm. The bilayer film has a thickness ratio of polymer to metal close to 11:1. The adhesion between PAA/PAH film and the aluminum layer is sufficiently strong to ensure an intimate contact between them because there are coordination interactions between carboxylate and amine groups in the PAA/PAH film and aluminum layer. The AFM top-view image in Figure 2b indicates that the evaporated aluminum layer has a granular surface with particle size close to 50 nm. Some of the particles coalesce together. The metal layer with granular structure was proved to enhance the sensitivity of the bilayer microcantilever sensors because it could result in a relatively larger tensile stress upon external stimulus than that with continuous morphology.[33]

The response of a strip of the bilayer Al/(PAA/PAH)*30 film with a size of 0.4 × 0.9 cm^2 to humidity changes was measured. The strip, with the polymeric PAA/PAH film on the top, was stuck with one side on a filter paper. As shown in Figure 3a, the course of the bending/unbending movements was recorded by a digital video camera recorder (DCR) with the decrease/increase of environmental humidity. At room temperature (25 °C) with a humidity of 12% RH, the strip was nearly flat with a slightly curving configuration from polymer film to metal layer. The prebent state is attributed to the deposition of the aluminum layer which induces the usual residual tensile stresses on the PAA/PAH polymer film.[34] When the strip was exposed to a gentle dry nitrogen flow (the rate of nitrogen flow is 0.2 m^3 h^{-1}) and the humidity decreased from 12% RH to 5% RH, it bent upward due to the contraction of the upper polymer film in the drier condition, as shown in the top row of Figure 3a. When the environmental humidity decreases, water molecules in the polymeric PAA/PAH film are lost, resulting in the contraction of the polymer film. The rigid aluminum layer is inert to moisture, and the dimension of the rigid aluminum layer keeps almost constant under the decreased environmental humidity. Therefore, the large mismatch in extraction leads to an interfacial stress between aluminum and PAA/PAH layers which bends the bilayer Al/(PAA/PAH)*30 film upward (i.e., bending toward the PAA/PAH film) when the humidity decreases. In the initial 8 s, the strip did not show observable bending movement. A delaying time exists for the bending of the bilayer film because the initial interfacial stress produced by the water desorption from the PAA/PAH film is not large enough to bend the film. An obvious bending of the bilayer film was observed after 10 s of nitrogen flowing. The bending movement continues as time elapses. It took about 46 s for the bilayer Al/(PAA/PAH)*30 film to

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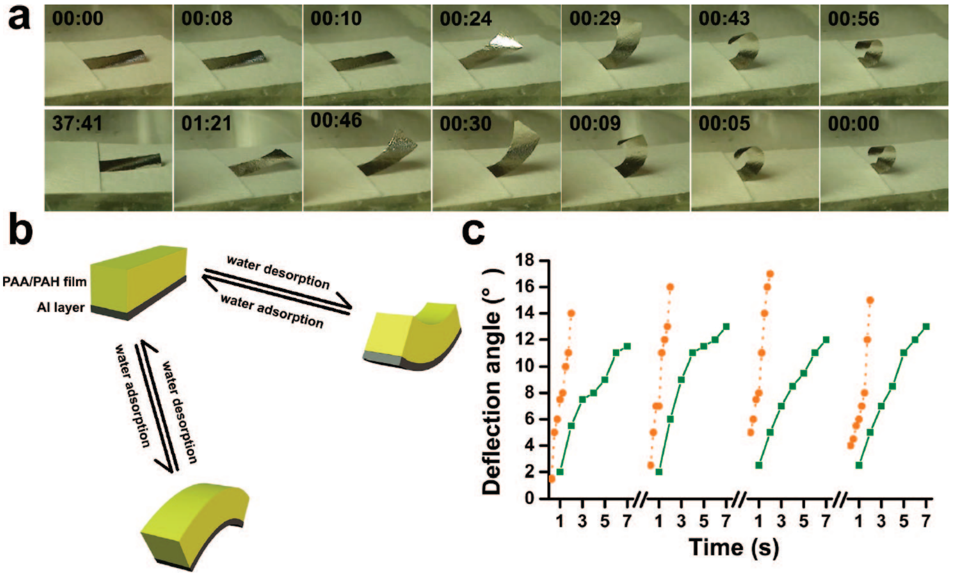

Figure 3. (a) Time profiles of bending and unbending movement of a bilayer Al/(PAA/PAH)*30 strip (0.4 × 0.9 cm^2) under different relative humidity conditions while the temperature was kept constant. The relative humidity in the top row changed from 12% RH to 5% RH and the low row from 5% RH to 12% RH. (b) Schematic illustration of the bending/unbending movement of a bilayer Al/(PAA/PAH) film toward humidity changes. (c) Time-dependent bending angles of a Al/(PAA/PAH)*30 film when the relative humidity changed from 12%RH to 5% RH. The aluminum layer has a thickness of 157 ± 6 nm (solid line) and 59 ± 4 nm (dotted line), respectively.

proceed from obvious bending movement to a nearly closed circle. With the stop of N_2 flow, the environment restored to the original humidity of 12% RH. The bilayer film underwent an unbending movement and relaxed to its original configuration, as depicted in the bottom row of Figure 3a. The unbending movement is due to the extension of the polymeric PAA/PAH film upon adsorption of water. Compared with the bending movement, the unbending process is relatively slow. The schematic illustration of the bending/unbending process with the change of environmental humidity is shown in Figure 3b. On the basis of the same principle, the bilayer Al/(PAA/PAH)*30 film shown in Figure 3a at room temperature with a humidity of 12% RH bends downward (i.e., toward the aluminum layer) with an increase of the environmental humidity. An unbending process takes place when the humidity restores to the original 12% RH. The bending of the bilayer Al/(PAA/PAH)*30 film to nearly a circle can be repeated many times without damaging the film.

It is worth noting that the bending movement is highly reversible and reproducible. The multiple bending of the above strip (0.4 × 0.9 cm^2) was performed when decreasing the environmental humidity from 12% RH to 5% RH. Figure 3c shows the deflection angle of the strips versus the response time. The deflection was recorded when the strip was starting to bend (i.e., the delaying time was not included). In all cases, the strip with an aluminum layer of 157 ± 6 nm spends 7 s to reach a deflection angle of ~12°, confirming that the bending of the strip is highly reproducible (Figure 3c, solid curves). Moreover, the response time of the bilayer Al/(PAA/PAH)*30 film is dependent on the thickness of the aluminum layer. The Al/(PAA/PAH)*30 film with a thinner aluminum layer has a faster response toward humidity change. The deflection angle of a Al/(PAA/PAH)*30 strip with an aluminum layer of 59 ± 4 nm versus the response time with decreasing the humidity from 12% RH to 5% RH is indicated in Figure 3c (dotted curves). The length of the time required to reach a deflection angle of 12° for the strip with a thinner aluminum layer is less than 2 s. The delaying time decreases to 4 s. It took 6 s for the bilayer strip with a thinner aluminum layer to bend from flat configuration to a circle at 25 °C with a humidity decrease from 12% RH to 5% RH (the delaying time is not included). Upon humidity decrease, the polymeric PAA/PAH film produced an interfacial stress to bend the aluminum layer. The thinner aluminum layer requires a smaller force to bend it. Therefore, the bilayer Al/(PAA/PAH)*30 film with a thinner aluminum layer becomes more sensitive to humidity change than that with a thicker aluminum layer.

The bilayer metal/polymer film can respond to the temperature change due to the large mismatch of thermal expansion coefficient (α) and thermal conductivity between the PAA/PAH film and the aluminum layer. Meanwhile, the increased temperature can facilitate the removal of the adsorbed water from PAA/PAH film. Control experiments reveal that the thermally cross-linked (PAA/PAH)*30 free-standing film cannot undergo bending/unbending movement with temperature changes. The synergetic effect of temperature increase and humidity decrease can accelerate the bending movement of the Al/(PAA/PAH) films. As shown in the top row of Figure 4a, with the increase of temperature from 25 to 60 °C and the concomitant decrease of humidity from 12% RH to 5% RH, the Al/(PAA/PAH)*30 strip (0.5 × 0.7 cm^2, aluminum layer thickness of 157 ± 6 nm) bends toward the same direction (from metal to polymer) as in the case of only humidity decrease, but with an accelerated speed. Just within 12 s (delaying time included), the strip became perpendicular to the horizontal plane. The increased temperature can, on the one hand, expand the aluminum layer and, on the other hand, facilitate the water removal from PAA/PAH film and contract the polymer layer. The combination of temperature increase and humidity decrease

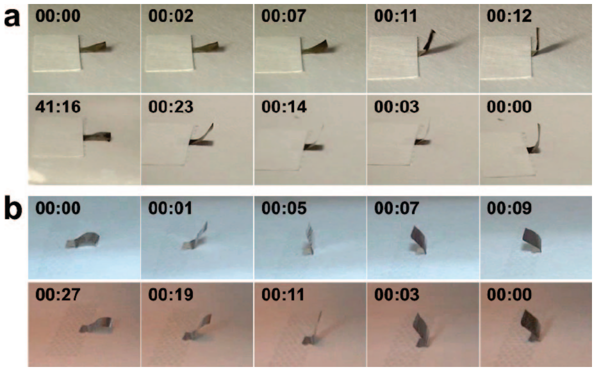

Figure 4. Time profiles of bending and unbending movement of a bilayer Al/(PAA/PAH)*30 strip (0.5 × 0.7 cm^2) with the change of temperature and relative humidity. (a) Top row: from 25 °C and 12% RH to 60 °C and 5% RH. Low row: from 60 °C and 5% RH to 25 °C and 12% RH. (b) Top row: from 4 °C and 78% RH to 60 °C and 5% RH. Low row: from 60 °C and 5% RH to 4 °C and 78% RH.

accelerates the bending movement and shortens the delaying time within 2 s. When the temperature decreased to 25 °C and the humidity increased to 12% RH, the unbending process takes place. The unbending process is still slow and takes about 40 min to fully relax the strip to a flat configuration. When the span of temperature and humidity change increases, the bending and unbending process of the Al/(PAA/PAH)*30 strip in Figure 3a can be further accelerated. Figure 4b depicts the bending and unbending process of the strip with a change between 4 °C with 78% RH and 60 °C with 5% RH. At 4 °C and 78% RH, the strip is not flat but with a slight curve profile from PAA/PAH polymer to Al layer. With the increase of the temperature to 60 °C and the decrease of humidity to 5% RH, the strip bends quickly. The bending to a perpendicular configuration takes ~4 s. It takes 27 s for the strip to relax to its original configuration when the environment restores to 4 °C and 78% RH. In this case, the delaying time is too short to exactly separate from the whole response process.

The humidity- and temperature-responsive property of the bilayer Al/(PAA/PAH) films can be used to mimic the blooming and senescence of morning glory flowers. As indicated in Figure 5, four pieces the of Al/(PAA/PAH)*30 free-standing film were stuck to a cubelike pillar, with the aluminum layer toward the outside. In a condition of 25 °C and 12% RH, the flower of the bilayer films is slightly open (Figure 5a). With the subsequent increase of temperature to 60 °C and decrease of humidity to 5% RH, the flower gradually closes (Figure 5b,c). Finally, when the temperature decreases to 4 °C and humidity increases to 78% RH, the flower of the bilayer films opens again, with a more blossomed state (Figure 5d). Herein, the environment in Figure 5a,d is humid with low temperature, similar to the situation of morning. While in Figure 5b,c, the temperature is high and humidity is low, mimicking the situation of noon.

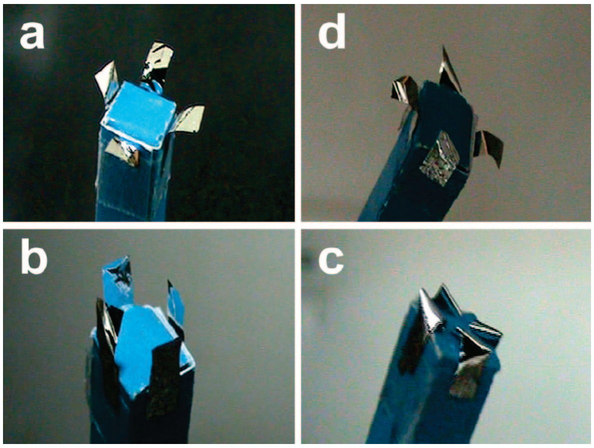

Figure 5. Images of a four-piece-strip Al/(PAA/PAH)*30 free-standing film stuck to a cubelike pillar under different temperature and humidity: (a) 25 °C and 12% RH, (b) 60 °C and 5% RH, (c) 60 °C and 5% RH after 20 s, and (d) 4 °C and 78% RH.

Conclusions and Outlooks

In conclusion, a humido- and thermo-responsive metal/polymer film was prepared in a facile way by evaporating nanoscale-thick aluminum layer on top of the thermally cross-linked LbL assembled free-standing PAA/PAH film. The bilayer Al/(PAA/PAH) film can undergo bending/unbending movements when the humidity and/or temperature of the environment changes. The bending/unbending movement of the bilayer films is caused by the large difference in response of the aluminum layer and the PAA/PAH polymeric film toward humidity and temperature. The bending behavior is largely related to the thickness of the aluminum layer. The bilayer Al/(PAA/PAH) film capable of bending/unbending under the change of environmental humidity and temperature can mimic the petals of morning glory flowers. Our studies confirmed that, besides aluminum, other kinds of metals such as gold, platinum, and so forth can also be used to design humidity- and temperature-responsive bilayer metal/polymer films. Meanwhile, the polymeric film is not limited to LbL assembled PAA/PAH. Most importantly, we believe that the flexibility of the LbL assembly technique for free-standing film fabrication allows the introduction of well designed recognition sites and enables the response of the bilayer films toward target substances. Therefore, the present study will provide a facile way to prepare novel responsive film materials toward not only humidity and temperature changes but also other types of stimuli and substances.

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