

Rapid Communication

Single-material Solvent-sensitive Fluorescent Actuator from Carbon Dots Inverse Opals Based on Gradient Dewetting*

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Abstract A novel solvent-sensitive fluorescent actuator with reversibility has been obtained from carbon dots (CDs) inverse opals, which is prepared *via* infiltrating CDs solution into the interstice of colloidal crystal template, thermal polymerization of CDs materials and removing the colloidal template. The as-prepared CDs inverse opal actuator shows a bending angle of 75° in 10.2 s, bending rate of 7.35 (°)·s⁻¹. In particular, the fluorescence intensity of the films varies during the actuating process. The actuating behavior is attributed to the inhomogeneous swelling/shrinking of the film, which originates from the gradient dewetting by solvent evaporation and hydrogen-bonding interaction between the solvent molecules and oxygen/hydrogen ions of CDs side chain. The CDs inverse opal actuator has the advantages of quick response, good repeatability and strong fluorescence, which gives an important insight into the design and manufacture of novel and advanced solvent-actuators.

Keywords Carbon dots inverse opal; Fluorescent; Single-material; Gradient dewetting; Solvent-actuator

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Many organisms in nature can produce a response to water or solvent in the environment^[1]. For example, the propagation of the seed of pinecones or wheat awns is maintained in a closed state in a moist environment, and when it is dry, the seeds are released. Inspired by these intelligent creatures in nature, dual-layer actuating materials capable of responding to external stimuli are prepared. These smart actuating materials can be mechanically stimulated by external stimuli, such as light^[2–8], electric field^[9, 10], humidity^[11–13], organic solvents^[14, 15], heat^[16–18] *etc.* Smart actuating materials have great potential applications in micro-robots^[19], artificial muscles^[20] and energy production^[11]. Recently, a new type of simple actuator derived from single materials^[11] or gradient^[12] has aroused great interest. Such an actuator can effectively overcome the limitation of bilayer actuator. As the special examples, Langer *et al.*^[11] developed a water-responsive polymer film which

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combined a rigid matrix (polypyrrole) with a dynamic network (polyol-borate) to fabricate a strong and flexible actuator. Yuan *et al.*^[12] described a porous polymer actuator with gradient structure and interaction between solvent molecules and actuator materials. In previous studies, we have prepared a single-material-based solvent-sensitive poly(ionic liquid) inverse opal actuator with a bending angle of 140° in 4 s^[21]. In this communication, we demonstrate a single-material-based solvent-sensitive fluorescent actuator from carbon dots inverse opal (CDIO). CDIO was fabricated *via* infiltrating CDs solution into colloidal crystal template, thermal polymerization of CDs materials and removing the colloidal template. The as-prepared CDIO actuator exhibits a bending angle of 75° in 10.2 s, bending rate of 7.35°s^{-1} , and the fluorescence intensity changes during the actuating process. It is attributed to the gradient wetting/dewetting behavior of the solvent in CDIO, together with the strong hydrogen bonding interactions between the side chain of CDs and the solvent. Furthermore, a fast response is achieved by the porous structure of inverse opal^[22–31] which can accelerate the internal mass transport and large-scale actuation arising from their high compressibility. This single-material actuator may provide an important insight into the design and fabrication of novel actuators.

CDIO was fabricated by the following procedures: dropping CDs solution (mixing CDs and ethanol at volume ratio of 1:1 into a hydrophilic photonic crystal (PC) template (plasma processing 60 s)) and then putting the infiltrated PC template at 80°C for 24 h. The free-standing CDIO film could be obtained by dissolving PC template in THF for 24 h. The film was cut into $0.8\text{ mm} \times 5\text{ mm}$ sheets for further usage. The as-prepared CDIO shows reversible actuating behavior based on gradient dewetting during the solvent evaporation process, as shown in Figs. 1(a) and 1(b). In Fig. 1(a), the solvent is dropped on the surface of CDIO to make the film straight and flat upon full solvent absorption. Then the film bends from one side accompanied with the solvent evaporation. With the increase of solvent evaporation, the bending angle of film grows. When the bending angle reaches a maximum, the value decreases gradually and restores to its original state due to the complete evaporation of solvent. Figure 1(b) demonstrates the whole actuation process. At first, the film keeps flat and straight state due to full wetting. And then the film bends and approaches the maximum bending angle of 75° in 10.2 s with a bending rate of 7.35°s^{-1} . Followed by the bending angle falls gradually toward a flat state, the film turns to the original flat state in 66.8 s. Figure 1(c) shows the chemical composition of CDs, which is mainly composed of graphene quantum dots containing various functional groups of organosilanes. Figure 1(e) presents SEM images of the as-prepared CDIO film. A clear periodic arrangement can be observed from the top-view. The thickness of the film is estimated to be about $3\text{ }\mu\text{m}$ from the side-view. CDIO also presented the unique structural color of colloidal crystal. The stopband positions of CDIO are 468, 612 and 723 nm with reflection of about 90%, indicating a good colloidal crystal structure, as shown in Fig. 1(f). The driving force of the actuating behavior mainly comes from the inhomogeneous swelling/shrinking of the film (Fig. 1d) based on gradient dewetting. The FTIR spectrum of the sample in Fig. S1 (in supporting information, SI) shows the unique characteristic peaks at 3279 , 2924 and 1095 cm^{-1} , corresponding to the vibrations of N–H, C–H and Si–O–Si groups respectively, which confirms the formation of CDIO.

Figure 2(a) presents the largest bending angle of as-prepared CDIO in different solvents. The definition of bending angle is shown in the inset of Fig. 2(a), which is the angle between the solid line and the dotted line. The linkage line is formed based on the tilted end of the sample and the support point. Clearly, the film shows different actuating behaviors when being removed from different solvents. Small bending angles were observed when the films were removed from toluene, acetone, chloroform and THF, while obvious bending behavior was found for the samples from ethanol and water with the bending angles of 75° and 41° respectively. The detailed actuating process of the film towards different solvents can be obtained in Fig. S2 (in SI). The *in situ* wetting/dewetting process^[32–35] of various solvents on the surface of CDIO was conducted. The results are shown in Fig. 2(b) and Fig. S3 (in SI), by which we can understand the distinct actuator behaviors towards different solvents. In the experiments, we monitored the contact angles (CAs) and the solvents' evaporation rates of the samples. It is found that the CAs are 93.5° , 14.6° , 14.5° , 13.5° , 12.9° and 10.4° for water, chloroform, toluene, acetone, THF and ethanol, respectively (Fig. 2b), indicating an increased wetting process and an enhanced interaction force between the solvent and polymer. Correspondingly, the solvents' evaporation time of

the samples are 1163, 53, 182, 28, 36, and 16 s for water, chloroform, toluene, acetone, THF, and ethanol respectively, implying a rough enhanced dewetting property for the solvents.

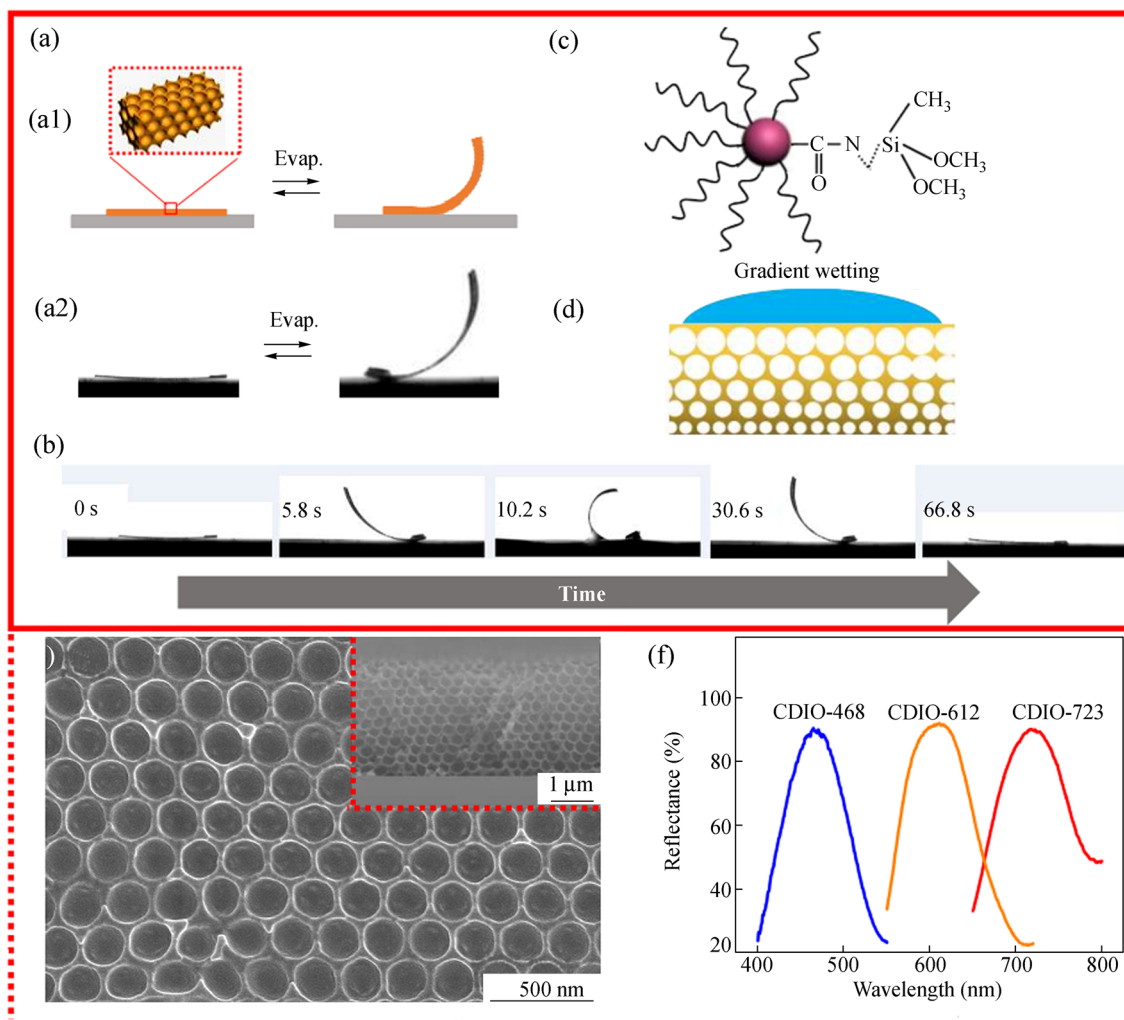


Fig. 1 (a) The schematic (a1) and relevant experiment photos (a2) of the actuating behavior of solvent-sensitive CDIO based on a wetting/dewetting process; (b) *In situ* images of a typical actuation process of the fully wetted sample based on gradient dewetting; (c) The chemical composition of carbon dots; (d) Schematic for the changing of microstructure resulted from gradient wetting; (e) The top-view and side-view (inset) SEM images of carbon dots inverse opal; (f) Reflection spectra of carbon dots inverse opal with different bandgaps

The decreased bending angle of the sample out of the various solvents can be attributed to the increased wetting/dewetting phenomenon (Fig. 2a). The basic driving force for the actuator is an inhomogeneous swelling/shrinking of the sample, which is aroused from a relatively slow wetting/dewetting process. In contrast, a rapid wetting/dewetting process prefers a homogeneous swell/deswell mode rather than an inhomogeneous swelling/shrinking, which cannot cause an obvious actuating behavior. Because of non-dissoluble/non-swelling of the solvent to the polymer, little actuating behavior could be observed when the sample was removed from toluene, acetone, chloroform and THF. In contrast, a better swelling but non-dissoluble property was found for the polymer in ethanol and water. In this case, the actuating property of single-material actuator mainly depends on the gradient wetting/dewetting, which induces an inhomogeneous swell/deswell and triggers the actuation action of corresponding polymer.

Notably, the actuation behavior of CDIO can be improved using a mixed solvent of water and ethanol, as shown in Fig. 2(c) and Fig. S4 (in SI). The bending angles change to 41° , 12.8° , 19.6° , 82.8° , and 75° when the ethanol volume ratio in water is 0%, 30%, 50%, 70%, and 100%, respectively. The largest bending angle is 82.8° in the 70% ethanol-water system, where the presence of water enhances the hydrogen bonding interactions between the solvent molecules and the oxygen/hydrogen ions in the side chain of CDs. While the presence of ethanol shortens the evaporation process, it provides an additional driving force for the bending process of the sample, which relieves the effects of gravity and resistance force during the bending process.

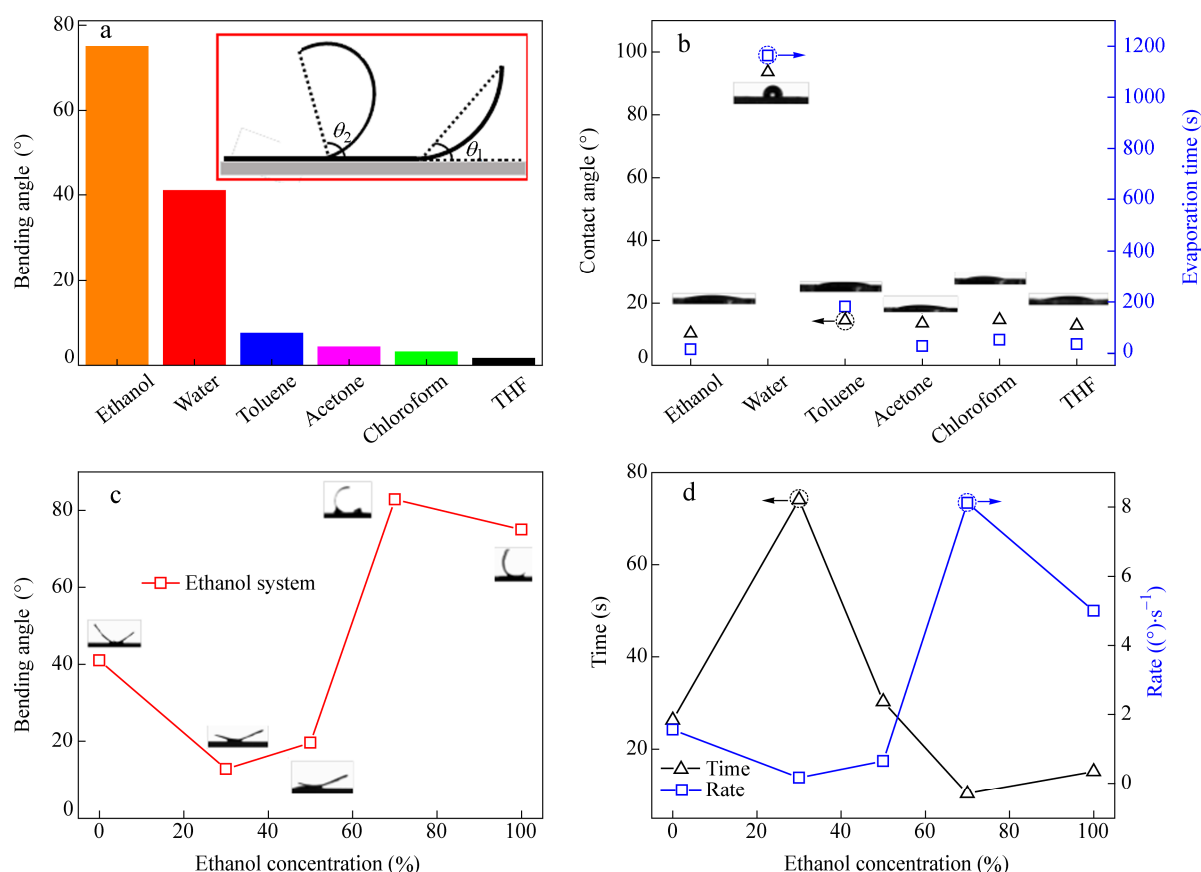


Fig. 2 (a) The largest bending angle of the sample in different solvent systems (Bending angle was calculated as shown in the inserted scheme); (b) The contact angle and the evaporation time of various solvents on the sample; (c) The largest bending angle of the sample in different proportion of ethanol and water systems; (d) The time taken for the sample approaching the largest bending angle in different proportion of ethanol and water systems and the corresponding rates

Similarly, the actuation rate of the samples is affected by mixed solvent system, as shown in Fig. 2(d). The actuation rate is characterized by the time to reach the largest bending angle, or the obtained bending angle in 1 s. When the ethanol volume ratios in water are 0%, 30%, 50%, 70%, and 100%, the actuation time change to 26.3, 74.1, 30.3, 10.2 and 15.1 s respectively, and the actuation rates shift to 1.56, 0.17, 0.65, 8.12 and 5.1 ($^\circ$)·s⁻¹. According to the experimental results, the fastest rate of actuator can be achieved when the ethanol volume ratio in water is 70%. The increase of ethanol results in the increased evaporation rate, which accelerates the dewetting process and is favorable for the gradient dewetting, while further increase of ethanol ratio weakens the hydrogen bonding interaction between the polymer chains and solvent molecules. Accordingly, selection of an appropriate solvent system is very important for the resulting application performance of actuator materials.

CDs is a novel carbon emitting material, which has excellent luminescent property from its excitation wavelength-dependent photoluminescence behavior and the broadband optical absorption^[36–38]. Figures 3(a) and

3(b) show the fluorescence change spectra, and Figs. 3(c) and 3(d) give the fluorescence images of the sample at the maximum bending angle during CDIO's actuating process excited at 480 and 560 nm. The fluorescence intensity increases with the enhancement of bending degree, and the maximum fluorescence intensity is not obtained until the maximum bending degree is reached. Subsequently, when the film returns to its original state, the fluorescence intensity gradually decreases. It can be seen more clearly from the fluorescent images (Figs. 3c and 3d, and Fig. S5 in SI) that the fluorescence intensity increases during the actuating process. At the beginning of actuating process, the film is in the swollen state compared with the dry film, causing the enhancement of the fluorescence intensity^[39]. With the evaporation of solvent, the swelling degree of film decreases gradually, which leads to the decrease of fluorescence intensity. The change of fluorescence intensity during actuating process can be used as an indicator for this process and has a potential application in the optical field. Figure 3(e) shows that the actuators can retain the reversibility for more than 6 cycles which may broaden its application in reality.

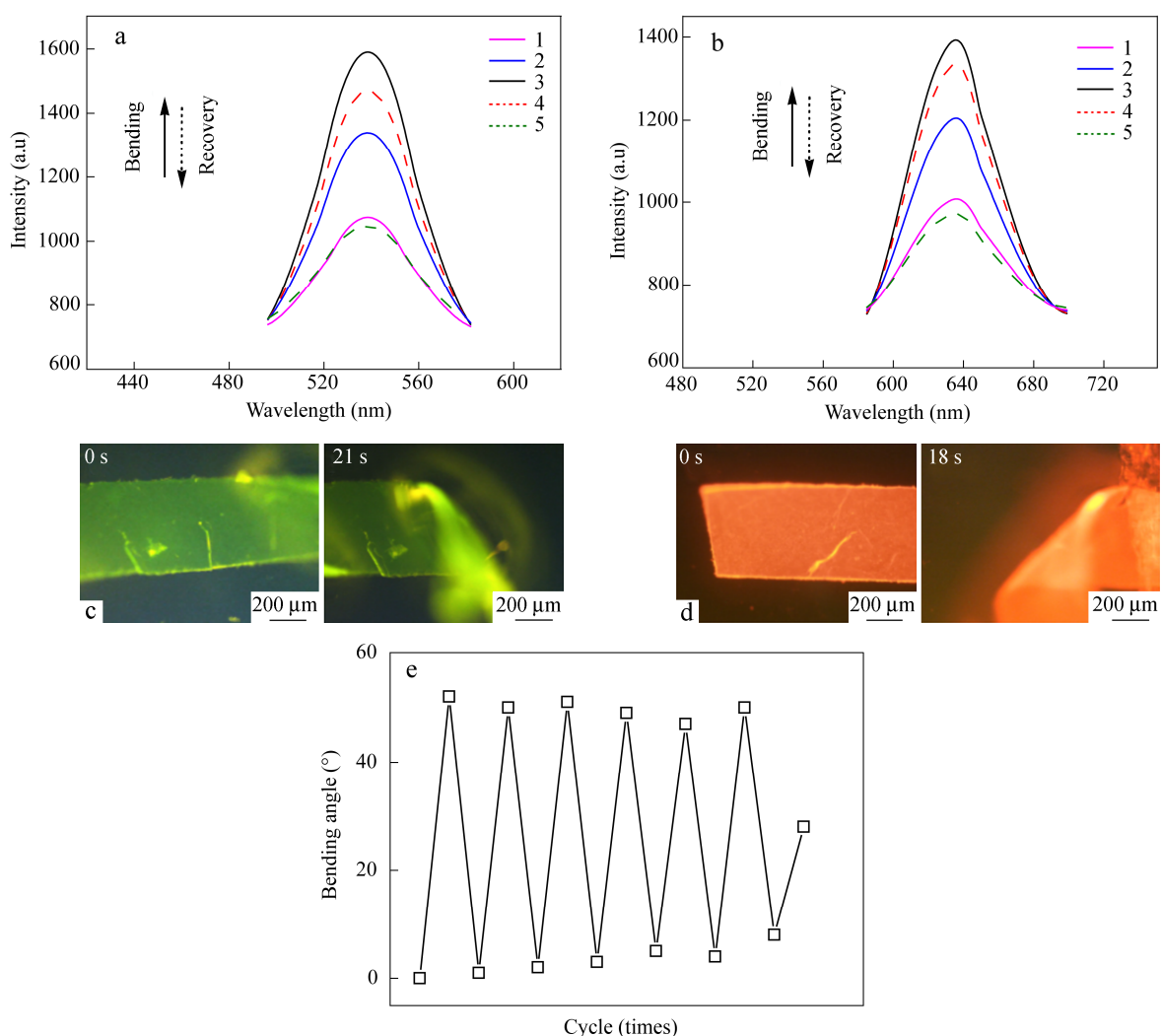


Fig. 3 (a, b) The fluorescence spectra and (c, d) fluorescence images of the sample at the maximum bending angle during the actuating process excited at (a, c) 480 and (b, d) 560 nm; (e) The reversible transition properties of CDIO actuator upon the gradient wetting/dewetting process

Figure 4(a) shows a possible explanation of the actuating process. Firstly, the solvent is dropped onto the as-prepared CDIO (Fig. 4a1), and then the sample is fully swollen by the solvent (Fig. 4a2). Subsequently, the

gradient dewetting forms due to the solvent evaporation, producing the shrinkable, partly-shrinkable and non-shrinkable region (Fig. 4a3) from upper to lower part. Such inhomogeneous shrinkage results in the actuator formation, and the sample curves up (Fig. 4a4). In other words, the actuating behavior is mainly aroused from the inhomogeneous swelling/shrinking due to the gradient dewetting process of solvent from the sample, as shown in Fig. 4(a3). The non-wetting part keeps an entanglement frozen state^[40–42] compared to an elastic network structure where polymer segment is wetted by the solvent, and hydrogen bonding interaction is formed between polymer and solvent molecules. Tensile is produced between the top dewetting part and the bottom wetted part based on the inhomogeneous swell/deswell of the bulk polymer segment, which causes an upward/downward bending of the sample. The gravity can be overcome by the inhomogeneous swelling/shrinkage so that the film can be actuated. A possible explanation for the different bending behaviors of CDIO is shown in Figs. 4(b)–4(h). First, the strong hydrogen-bonding is formed between the side chain of CDs and solvent molecules when the sample is swollen by the solvent, as shown in Fig. 4(b). Upon solvent evaporation, the frontier of liquid retracts from the upside/top part to the middle/bottom part of the film, causing a shrinkable state starting from the upper/side to the bottom/center part, inducing an upward bending of the sample. The convective flow leads to a tractive force that moves along the frontier of the liquid. The film enhances its bending angle with further solvent evaporation. The gravity and deformational force can be overcome by the tractive force during the actuating process. Therefore, the film shows an actuating behavior. Finally, the film reverts to the original flat state when the tensile force decreases/disappears due to the fact that inhomogeneous dewetting turns to a homogeneous drying. It is noted that the film can be pinned on the substrate during the actuating process because of a strong capillary force between the film and substrate. More importantly, gradient dewetting may be achieved due to the strong capillary which slows the solvent evaporation in the lower part of film.

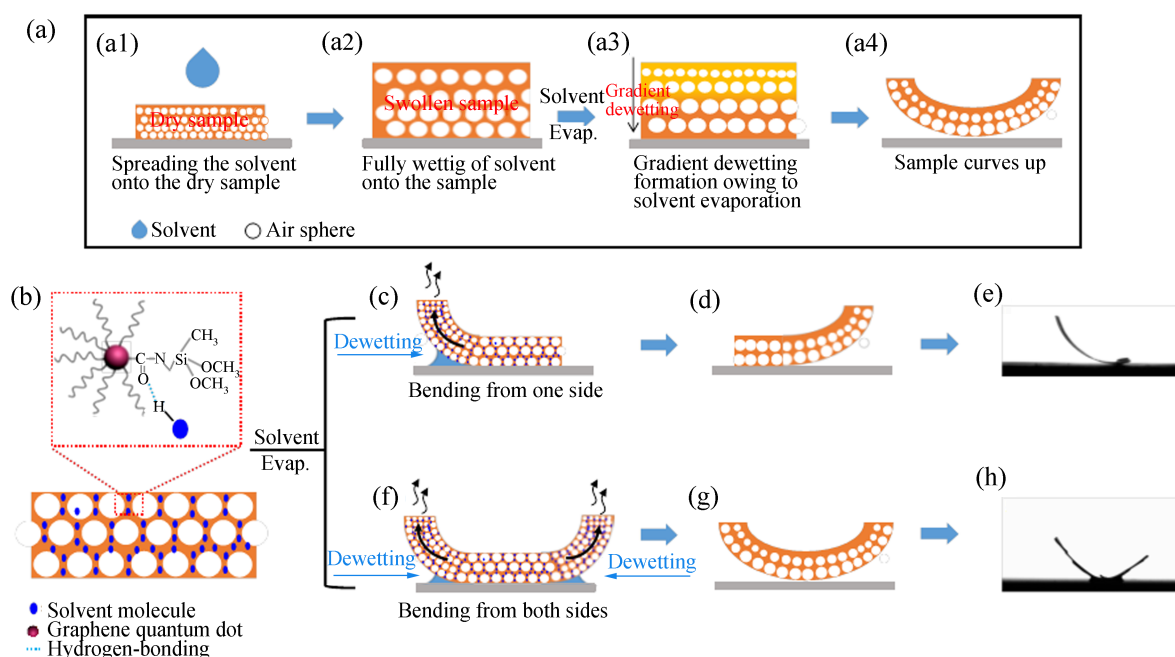


Fig. 4 (a) Scheme illustration for the actuator process of the single-material-based solvent-sensitive actuator (The four existing states of the sample (from left to right): dry sample, fully swollen, gradient dewetting (gradient swollen) and curving sample); (b) A detailed schematic of the fully swollen state (Strong hydrogen bonding exists between the solvent and polymer segment.); (c, f) The two types of dewetting states of the sample, (d, g) the corresponding deformations and (e, h) the corresponding experiment photos of the sample

Moreover, two bending situations have been found in the experiment, as shown in Figs. 4(c)–4(h). The bending starts from the film ends. The position of tractive force determined by the varied dewetting cases and the convective flow interaction play an important role in the different bending situations. The tractive force is firstly generated at the film ends owing to the fast evaporation flow there, resulting in a corresponding dewetting, fast shrinkage and an upward bending from one/two end(s) of the film. With the evaporation of solvent, an enhanced bending is achieved due to further shrinkage of the sample, as shown in Figs. 4(d) and 4(g).

In conclusion, a single-material-based reversible solvent-response fluorescence actuator is obtained from CDIO based on a gradient wetting/dewetting process. The sample demonstrates distinct actuating behavior when solvent is evaporated from it, which gives an important insight for the design of novel and advanced solvent-actuators.

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