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3D Printed Photo-responsive Devices Based on Shape Memory Composites

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Stimuli-responsive devices are eliciting widespread interest due to their ability to sense and then act according to a pre-determined sequence when triggered by external stimuli such as heat, light or electricity, which arises from the conformational changes of their constituent stimuli-responsive polymers.^[1-19] Meanwhile, three-dimensional (3D) printing is able to endow devices with complex geometries of precisely prescribed microarchitectures, in order to satisfy individual needs and requirements.^[20-35] In comparison to traditional stimuli-responsive devices with simple planar or tubular geometries, such as actuators and stimuli-responsive films fabricated by spin-coating, casting or extrusion,^[36-40] 3D printed stimuli-responsive devices not only intimately meet the requirement of complicated shapes at macro-level, but also satisfy various conformation changes triggered by external stimuli at the microscopic scale.^[41-45] Thus, these 3D printed stimuli-responsive devices may shape the future trends and opportunities of device development in various fields ranging from biomedical devices to soft robots. However, the development of such 3D printed stimuli-responsive devices is limited by the lack of 3D printing functional materials. Currently, most of such devices are fabricated based on thermal-responsive shape memory polymers, such as polycaprolactone (PCL) synthesized through 3D photopolymerization printing of polycaprolactone macromonomer, which exhibit a mechanical response when triggered only by heat.^[41-45] Thus, the design and fabrication of 3D printable other stimuli-responsive

devices, such as humidity, chemical, or light responsive devices, remains a great challenge and opportunity for highly customized wearable sensors, soft robotics, and medical devices.

Alternatively, light as an external trigger is attracting notable interest on account of its capability for remote control, accurate focusing, and rapid switching of properties, especially sunshine that possesses green and sustainable merits.^[46-47] It is possible that light could be considered as an attractive trigger to control the stimuli-responsive behavior of 3D printable devices. However, progress in 3D printable photo-responsive devices remains limited by the incompatibility between current 3D printing technology and photo-responsive materials. 3D photopolymerization printing, which is frequently used to construct 3D printed thermal-responsive devices, is not desirable for printing photo-responsive materials as the photo-responsive groups of functional materials can undergo significant conformation or structure transitions when exposed to UV illumination during the 3D printing process.^[46-50] Typical transitions induced by UV illumination include the dipole moment, size and shape changes of azobenzene groups, zwitterionic species formation of spirobenzopyran groups, charge generation of triphenylmethane leucohydroxide groups, and photodimerization of cinnamoyl groups.^[51-52] When materials comprising these photo-responsive groups are used to fabricate 3D printable photo-responsive devices through photopolymerization, the aforementioned transitions in the 3D printing process can lead to remarkable changes in the optical, mechanical and chemical properties of the photo-responsive devices. As a result, both the rational design of photo-responsive materials and the selection of appropriate 3D printing technology are essential for 3D printable photo-responsive devices.

Comparing with 3D photopolymerization printing technology, fused deposition modeling (FDM) is a type of 3D printing technology that does not require exposure to UV light. FDM can be chosen to fabricate 3D printable photo-responsive devices, avoiding the significant influence of UV illumination in 3D printing process.^[53-57] Currently, only a few thermoplastic polymers such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS),

and polycarbonate (PC) are employed for FDM to print durable devices with advantages in mechanical property, chemical resistance and thermal stability.^[58-59] In order to fabricate 3D printable photo-responsive devices by FDM, smart polymers polyurethane (PU) are catching our attentions on account of their dynamic shape memory property and advisable melting temperature. The shape recovery ability of PU from the deformed state to the original shape makes 3D printable devices to sense and then act according to a pre-determined sequence when triggered by external stimulus. In addition, the advisable melting temperature of thermoplastic polymers PU ($< 260\text{ }^{\circ}\text{C}$, the maximum working temperature of commercial FDM printer) makes them possible for FDM to print 3D shape memory devices. Moreover, due to the excellent photo-thermal conversion efficiency of carbon black ($92 \pm 3\%$),^[60-61] the addition of carbon black (CB) into PU endows 3D printable shape memory devices with photo response. Thus, we hypothesized that shape memory polymers PU and photo-thermal conversion materials CB can be mixed to prepare photo-responsive shape memory composites PUCB (**Scheme 1a**) as 3D printing materials for FDM to fabricate 3D printable photo-responsive shape memory devices through layer-by-layer deposition.

First of all, we successfully demonstrated the 3D printing of a $30 \times 30 \times 30\text{ mm}$ cubic with $4 \times 4\text{ mm}$ frame with photo-responsive shape memory behavior using PUCB as printing materials by commercial FDM printer. The printing of such a frame resembling the crystal structure of NaCl by FDM printer constitutes a huge challenge due to the hollow and overhanging components of the structure. When the temperature of nozzle is above the melting point of PUCB, the thermoplastic filament would be in the melt state, thus enabling its extrusion from the nozzle for printing cubic frame by a commercial FDM printer (**Scheme 1b**).^[62] After heating, adding external force, and cooling for 3D printed cubic frame, the temporary shape of the cubic frame was fixed from the original state (**Figure S1**, Supporting Information). Remarkably, the shape recovery of 3D printed cubic frame from the temporary to the original shape is able to be triggered by external illumination (**Scheme 1c**) due to photo-

responsive shape memory property of printing materials PUCB. After 160 s of illumination, the cubic frame fully recovered from the squashed state to the three-dimensional state (**Figure 1a**, and Movie S1, Supporting Information). In addition, we demonstrated that natural sunlight of intensity 76 mW cm^{-2} (Figure 1b and Movie S2, Supporting Information) also triggered the shape memory behavior of our 3D printed cubic frame. The cubic frame was first fixated at a temporary shape (the squashed state), and then placed on the cobblestone road for the absorption of sunlight. Interestingly, after 160 s of illumination, the shape of cubic frame recovered to its original state, leading to the shape change from the squashed state to the 3D state (Figure 1b). It indicates that mere sunlight can also trigger the shape memory behavior of these 3D printed devices fabricated by the integration of PUCB and FDM, which may extend their applications in the fields of biomimetic solar tracking sensors and smart solar cell systems.

To choose an optimal weight ratio of CB to PU for printing 3D photo-responsive devices by FDM, we studied the thermal curves of 3D printing materials when exposed to light by the infrared thermal perturbation method. Circular films of diameter 10 mm and thickness 0.6 mm were fabricated from PUCB with different weight ratios of CB to PU, and a 300 W Xenon light source was used to mimic sunlight. With the increase of illumination under a light intensity of 60 mW cm^{-2} from 0 to 900 s, the temperature of the film with different weight ratio of CB to PU increased (**Figure 2a**) due to the photo-thermal function of CB. When the weight ratio of CB to PU was increased from 0 to 15%, the maximum temperature increased from 29.3 to 40.5 °C (Figure S2, Supporting Information). It indicates that the addition of CB increased the maximum temperature that the photo-responsive composites reached under the same conditions. In addition, the increase of the weight ratio of CB to PU can decrease the glass-transition temperature T_g of 3D printing materials (Figure S3, Supporting Information). Thus, we can design and fabricate photo-responsive printing materials with different shape memory behavior triggered by light through adjusting the

weight ratio of CB to PU in materials. As the printing of filaments with diameter of 1.75 mm is favorable for the standard FDM printer, the photo-responsive composites with 10 wt% of CB to PU is preferential for the printing of photo-responsive shape memory devices as it can be extruded to the desired diameter with our extruder.

To further understand the mechanism of photo-responsive shape memory behavior, we performed control experiments on circular films printed by FDM with PUCB comprising 10 wt% of CB, which are of diameter 10 mm and thickness 0.6 mm. After 1200 s of illumination under a light intensity of 32 mW cm⁻², the temperature of 3D printed film increased from room temperature to a maximum temperature of 33.4 °C (Figure 2b). With the subsequent removal of the light source, the temperature of the 3D printed film recovered to room temperature after 990 s. This indicates that 3D printed devices effectively generated heat from absorbed light, which was used to drive shape recovery from the temporary to the original shape. In addition, the maximum temperature was increased from 33.4 to 46.1 °C with the increase of light intensity from 32 to 87 mW cm⁻². This indicated a positive relationship between light illumination intensity and the heat generated by our 3D printed devices, which effectively influenced the light-triggered shape memory behavior. Based on the photo-thermal conversion curves as shown in Figure 2b, the external photo-thermal efficiency η_{ext} of our shape memory materials was calculated by the following equations, as reported by our previous work^[63]:

$$\eta_{ext} = \frac{Q}{q} \quad (1)$$

Where Q is the generated heat, and q is the irradiation energy of photon flux.

$$Q = Q_{surr}^{max} = hs(T_{max} - T_{surr}^{max}) \quad (2)$$

where h refers to the heat transfer coefficient, and s is the surface area for heat dissipation.

The external photo-thermal efficiency η_{ext} was calculated by combining Equation (1) and (2).

Figure 2c showed the average external photo-thermal efficiency of 3D printing materials was

about 13% under different light intensity, which was reasonable as only 10% of the 3D printing material (the CB component) effectively absorbed light to generate heat (Figure 2c). In addition, differential scanning calorimetry (DSC) revealed that T_g of PUCB with 10 wt% of CB was 30 °C (Figure 2d), which was lower than the maximum temperature obtained through photo-thermal conversion. These experimental data display that CB can absorb external light to increase the temperature of PUCB above its glass-transition temperature, leading to the shape memory behavior of 3D printed devices triggered by light.

To quantify the effect of materials thickness and light density on shape memory behavior, we printed 40 × 20 mm PUCB films (**Figure 3a**) of different thicknesses (Movie S3, Supporting Information). The shape memory behavior of these 3D printed films was systematically studied via the following steps (Figure S4, Supporting Information). First, the 3D printed films were kept in their original shape for 10 min in a 70 °C water bath ($> T_g$). Second, the 3D printed films were bent into a temporary shape with a 40° deformation angle α (defined as shown in Figure 3b) and then kept 10 min in ice-water bath ($< T_g$), thus fixating the elastic deformation. Third, the 3D printed films were removed from the ice-water bath and subsequently illuminated by the light source. Fourth, the process in which the 3D printed films recovered their original shape was recorded in order to study the effect of film thickness on the shape memory behavior in detail. It can be observed that the α of 3D printed films increased with the illumination time. When the light intensity is 198 mW cm⁻², the α of a 0.6 mm 3D printed films increased from 40 to 180° after 180 s of illumination. This indicates that 3D printed film has a photo-triggered shape memory property. In addition, with increasing film thickness from 0.4 to 1.0 mm, the α of the 3D printed films decreased from 170 to 130° after 90 s of illumination (Figure 3c). This indicates that an increase in film thickness would prolong the shape memory time of 3D printed devices, as a thicker film would inhibit the heat conduction in the materials. Next, we chose 3D printed films of thickness 0.6 mm to study the effect of light intensity on the shape memory behavior of the

3D printed films. When the light intensity was reduced from 198 to 32 mW cm⁻², the illumination time taken for the 3D printed film to increase from 40 to 135° is extended from 180 s to 420 s (Figure 3d). As a control experiment, the α of 3D printed film without illumination remained unchanged with the increase in time. It further confirms the photo-triggered shape memory property of the 3D printed film. The reduction in shape recovery time of 3D printed devices with a stronger light intensity can be attributed to the increase in light absorbed by the CB component of the material, which enables it to generate more heat energy. The aforementioned results show that both light intensity and illumination time influence the shape memory behavior of these 3D printed films. The relationship in deformation angle α , illumination time t and light intensity I can be summed up through the following empirical equation (details as shown in Supporting Information), which characterizes the deformation angle as a function of illumination time and light intensity:

$$\alpha = \frac{A_1 \cdot \exp(B_1 I) + A_2 \cdot \exp(B_2 I)}{1 + \exp\left\{-(C_1 I + C_2) \cdot t + \ln\left[\frac{A_1 \cdot \exp(B_1 I) + A_2 \cdot \exp(B_2 I)}{D_1} - 1\right]\right\}} \quad (3)$$

in which A_1 is 1.458×10^2 , A_2 is -1.057×10^2 , B_1 is 1.05×10^{-3} , B_2 is -5.637×10^{-2} , C_1 is 3.57×10^{-4} , C_2 is 9.778×10^{-3} , and D_1 is 40. Based on equation (3), the deformation angle fitted curves with increasing illumination time of 3D printed films under different illumination intensities can be obtained, which match well with that obtained by experiments (Figure S5, Supporting Information). In addition, we obtained a contour map detailing the changes in the deformation angle with both illumination time and light intensity (Figure 3e), which would render it convenient for researchers to study the photo-responsive shape memory property of our materials.

It is well known that plants such as sunflowers exhibit heliotropism, which is the ability to move in response to sunlight due to photo-responsive hormones called auxins in the stem.^[64] Due to the sensitivity of these hormones to sunlight, sunflowers do everything to avoid sunshine, leading which manifests as the growth of cells in the shaded region and make

sunflowers phototropism bending and moving with sunshine.^[65] Inspired by the heliotropism of sunflowers (**Figure 4a**), photo-responsive shape memory sunflower was fabricated by combining commercial FDM printer and active materials PUCB. The petals of sunflower were printed by black photo-responsive shape memory materials PUCB, while the stamen, pedicel and vase of sunflower were printed by polylactic acid. These parts were assembled to form an integrated photo-responsive shape memory sunflower (**Figure 4b**). With the increase of the temperature of sunflower to above T_g (30 °C), the petals of sunflower is converted from the rigid state to an elastomeric and pliant state. When the temperature of the sunflower is below T_g , any deformation of sunflower formed by application of external force can be fixated; as an example, the sunflower was given a temporary shape in the form of closed petals (**Figure 4b**). **Figure 4c** shows the different deformation states of the sunflower at different illumination times under a light intensity of 87 mW cm⁻², which was obtained every 40 s. As the illumination time increases, the shape of sunflower petal would eventually recover to its original state, resulting in a shape change from the closed to the open state. This process is similar to that of an actual sunflower when it goes from bud to bloom. After 280 s of illumination, full blooming of the sunflower was achieved (**Movie S4**, Supporting Information). The photo-thermal conversion of 3D printed sunflower was subsequently studied by infrared thermal perturbation method. It can be seen that prior to illumination, the temperature of sunflower was 0.4 °C (**Figure 4d**), which is much lower than T_g , thus enabling the sunflower to retain its closed state. After 280 s of illumination, the CB component of the sunflower material would generate heat from the absorbed light, causing the temperature of the sunflower to increase from 0.4 to 34.4 °C (**Figure 4e**). The temperature 34.4 °C is higher than T_g of the sunflower, thus triggering its flowering process. In this way, we printed 3D printed sunflower with light-triggered shape memory behavior, which is similar to the heliotropism of plants.

In summary, we fabricated 3D printed photo-responsive shape memory devices through combining FDM printing technology and photo-responsive shape memory composites based on PU and CB. FDM is applied to avoid the influence of UV illumination in the 3D printing process of photo-responsive devices. The addition of CB with an efficient photo-thermal conversion endows our 3D printed shape memory devices with excellent photo response. Interestingly, natural sunlight can also trigger the shape memory behavior of 3D printed devices. The development of this facile printing strategy will provide tremendous opportunities for the design and fabrication of personal stimuli-responsive devices, which can be widely applied in the field of attractive and highly-personalized biomimetic smart devices and soft robotics.

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Reference

- [1] H. Yang, Z. Liu, B. K. Chandran, J. Deng, J. Yu, D. Qi, W. Li, Y. Tang, C. Zhang, X. Chen, *Adv. Mater.* **2015**, 27, 5593.

- [2] H. Wang, F. Meng, B. Zhu, W. R. Leow, Y. Liu, X. Chen, *Adv. Mater.* **2015**, 27, 7670.
- [3] H. Yang, D. Qi, Z. Liu, B. K. Chandran, T. Wang, J. Yu, X. Chen, *Adv. Mater.* **2016**, 28, 9175.
- [4] S. Han, Y. Zhou, V. A. L. Roy, *Adv. Mater.* **2013**, 25, 5425.
- [5] J. G. Hardy, M. Palma, S. J. Wind, M. J. Biggs, *Adv. Mater.* **2016**, 28, 5717.
- [6] Y. Liu, K. Xu, Q. Chang, M. A. Darabi, B. Lin, W. Zhong, M. Xing, *Adv. Mater.* **2016**, 28, 7758.
- [7] B. Zhu, H. Wang, W. R. Leow, Y. Cai, X. J. Loh, M.-Y. Han, X. Chen, *Adv. Mater.* **2016**, 28, 4250.
- [8] Y. Qian, X. Zhang, L. Xie, D. Qi, B. K. Chandran, X. Chen, W. Huang, *Adv. Mater.* **2016**, 28, 9243.
- [9] P. Wan, X. Chen, *ChemElectroChem* **2014**, 1, 1602.
- [10] T. Xie, *Nature* **2010**, 464, 267.
- [11] X. Li, M. J. Serpe, *Adv. Funct. Mater.* **2016**, 26, 3282.
- [12] T. Wang, Y. Guo, P. Wan, H. Zhang, X. Chen, X. Sun, *Small* **2016**, 12, 3748.
- [13] M. Behl, K. Kratz, J. Zotzmann, U. Nöchel, A. Lendlein, *Adv. Mater.* **2013**, 25, 4466.
- [14] M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, 9, 101.
- [15] D. Qi, Y. Liu, Z. Liu, L. Zhang, X. Chen, *Adv. Mater.* **2017**, 29, 1602802.
- [16] K. Ariga, J. Li, J. Fei, Q. Ji, J. P. Hill, *Adv. Mater.* **2016**, 28, 1251.
- [17] Y. Tokoro, K. Tanaka, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2015**, 88, 1350.
- [18] H. Xie, M. He, X. Deng, L. Du, C. Fan, K. Yang, Y. Wang, *ACS Appl. Mater. Interfaces*, **2016**, 8, 9431.
- [19] H. Tokoro, S. Ohkoshi, *Bull. Chem. Soc. Jpn.* **2015**, 88, 227.
- [20] Y. S. Rim, S. Bae, H. Chen, N. D. Marco, Y. Yang, *Adv. Mater.* **2016**, 28, 4415.

- [21] R. D. Farahani, M. Dubé, D. Therriault, *Adv. Mater.* **2016**, 28, 5794.
- [22] D. B. Kolesky, R. L. Truby, A. S. Gladman, T. A. Busbee, K. A. Homan, J. A. Lewis, *Adv. Mater.* **2014**, 26, 3124.
- [23] A. L. Rutz, K. E. Hyland, A. E. Jakus, W. R. Burghardt, R. N. Shah, *Adv. Mater.* **2015**, 27, 1607.
- [24] C. B. Highley, C. B. Rodell, J. A. Burdick, *Adv. Mater.* **2015**, 27, 5075.
- [25] B. G. Compton, J. A. Lewis, *Adv. Mater.* **2014**, 26, 5930.
- [26] M. Ebara, K. Uto, N. Idota, J. M. Hoffman, T. Aoyagi, *Adv. Mater.* **2012**, 24, 273.
- [27] J. T. Muth, D. M. Vogt, R. L. Truby, Y. Menguc, D. B. Kolesky, R. J. Wood, J. A. Lewis, *Adv. Mater.* **2014**, 26, 6307.
- [28] B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Y. Guo, S. I. Park, Y. J. Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers, J. A. Lewis, *Science* **2009**, 323, 1590.
- [29] H. Jiang, S. Kelch, A. Lendlein, *Adv. Mater.* **2006**, 18, 1471.
- [30] W. Guo, C. Lu, R. Orbach, F. Wang, X. Qi, A. Cecconello, D. Seliktar, I. Willner, *Adv. Mater.* **2015**, 27, 73.
- [31] Q. Ge, H. J. Qi, M. L. Dunn, *Appl. Phys. Lett.* **2013**, 103, 131901.
- [32] Q. Ge, C. K. Dunn, H. J. Qi, M. L. Dunn, *Smart Mater. Struct.* **2014**, 23, 094007.
- [33] D. Raviv, W. Zhao, C. McKnelly, A. Papadopoulou, A. Kadambi, B. Shi, S. Hirsch, D. Dikovsky, M. Zyracki, C. Olguin, R. Raskar, S. Tibbits. *Sci. Rep.* **2014**, 4, 7422.
- [34] S. E. Bakarich, R. Gorkin III, M. I. Panhuis, G. M. Spinks, *Macromol. Rapid Commun.* **2015**, 36, 1211.
- [35] Q. Zhang, D. Yan, K. Zhang, G. Hu, *Sci. Rep.* **2015**, 5, 8936.
- [36] H. Tobushi, S. Hayashi, K. Hoshio, Y. Ejiri, *Sci. Technol. Adv. Mater.* **2008**, 9, 015009.
- [37] D. Habault, H. Zhang, Y. Zhao, *Chem. Soc. Rev.* **2013**, 42, 7244.
- [38] Z. Li, X. Zhang, S. Wang, Y. Yang, B. Qin, K. Wang, T. Xie, Y. Wei, Y. Ji, *Chem. Sci.* **2016**, 7, 4741.

- [39] C. Zhu, C. Ninh, C. J. Bettinger, *Biomacromolecules* **2014**, 15, 3474.
- [40] Y-C Li, Y. S. Zhang, A. Akpek, S. R. Shin, A. Khademhosseini, *Biofabrication* **2017**, 9, 012001.
- [41] Y. Mao, Z. Ding, C. Yuan, S. Ai, M. Isakov, J. Wu, T. Wang, M. L. Dunn, H. J. Qi, *Sci. Rep.* **2016**, 6, 24761.
- [42] M. Zarek, M. Layani, I. Cooperstein, E. Sachyani, D. Cohn, S. Magdass, *Adv. Mater.* **2016**, 28, 4449.
- [43] A. S. Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan, J. A. Lewis, *Nat. Mater.* **2016**, 15, 413.
- [44] Y. Mao, K. Yu, M. S. Isakov, J. Wu, M. L. Dunn, H. J. Qi, *Sci. Rep.* **2015**, 5, 13616.
- [45] J. Wu, C. Yuan, Z. Ding, M. Isakov, Y. Mao, T. Wang, M. L. Dunn, H. J. Qi, *Sci. Rep.* **2016**, 6, 24224.
- [46] F. D. Jochum, P. Theato, *Chem. Soc. Rev.* **2013**, 42, 7468.
- [47] H. Yang, B. Yuan, X. Zhang, O. A. Scherman, *Acc. Chem. Res.* **2014**, 47, 2106.
- [48] H. Yang, Z. Ma, Z. Wang, X. Zhang, *Polym. Chem.* **2014**, 5, 1471.
- [49] S. Dai, P. Ravi, K. C. Tam, *Soft Matter* **2009**, 5, 2513.
- [50] X. Jiang, C. A. Lavender, J. W. Woodcock, B. Zhao, *Macromolecules* **2008**, 41, 2632.
- [51] M. Li, P. Keller, *Soft Matter* **2009**, 5, 927.
- [52] M. Wei, Y. Gao, X. Li, M.J. Serpe, *Polym. Chem.* **2017**, 8, 127. |
- [53] Y. Zhao, L. Tremblay, Y. Zhao, *Macromolecules* **2011**, 44, 4007.
- [54] P. J. Kitson, S. Glatzel, W. Chen, C. G. Lin, Y. F. Song, L. Cronin, *Nat. Protoc.* **2016**, 11, 920.
- [55] R. Matsuzaki, M. Ueda, M. Namiki, T. K. Jeong, H. Asahara, K. Horiguchi, T. Nakamura, A. Todoroki, Y. Hirano, *Sci. Rep.* **2016**, 6, 23058.
- [56] J. H. Kim, W. S. Chang, D. Kim, J. R. Yang, J. T. Han, G. Lee, J. T. Kim, S. K. Seol, *Adv. Mater.* **2015**, 27, 157.

- [57] T. D. Brown, P. D. Dalton, D. W. Hutmacher, *Adv. Mater.* **2011**, 23, 5651.
- [58] R. D. Farahani, K. Chizari, D. Therriault, *Nanoscale* **2014**, 6, 10470.
- [59] S. Shaffer, K. Yang, J. Vargas, M. A. Di Prima, W. Voit, *Polymer* **2014**, 55, 5969.
- [60] C. R. Rocha, A. R. T. Perez, D. A. Roberson, C. M. Shemelya, E. MacDonald, R. B. Wicker, *J. Mater. Res.* **2014**, 29, 1859.
- [61] Z. Wang, P. Tao, Y. Liu, H. Xu, Q. Ye, H. Hu, C. Song, Z. Chen, W. Shang, T. Deng, *Sci Rep.* **2014**, 4, 6246.
- [62] B. M. Behl, M.Y. Razzaq, A. Lendlein, *Adv. Mater.* **2010**, 22, 3388.
- [63] J. Wang, Y. Li, L. Deng, N. Wei, Y. Weng, S. Dong, D. Qi, J. Qiu, X. Chen, T. Wu, *Adv. Mater.* **2017**, 29, 1603730.
- [64] B. Hocking, D. Sharplin, *Nature* **1965**, 206, 206.
- [65] P. G. Kevan, *Science* **1975**, 189, 723.

Scheme 1. a) Photo-responsive shape memory behavior of 3D printing materials based on carbon black and PU. b) 3D printed device fabricated by fused deposition modeling. 3D printing materials are extruded from nozzle and moved in both horizontal and vertical directions by controlled stepper motors to print devices on a glass panel by layer-by-layer deposition. c) Photo-responsive shape memory behavior of 3D printed device.

Figure 1. The shape recovering process of cubic frame under (a) 87 mW cm⁻² of light source and (b) 76 mW cm⁻² of sunshine. First, a temporary shape of sunflower was fixated at the flat state. Then, it was able to absorb the sunshine to generate heat. The images were obtained every 40 s. At last, sunshine triggered the shape memory behavior.

Figure 2. a) Photo-thermal conversion of shape memory materials with different weight ratios of CB to PU under a light intensity of 60 mW cm^{-2} . b) The photo-thermal conversion curves of 3D printed film (10 wt% of CB to PU) with different light intensity. c) The external photo-thermal efficiency of 3D printing materials (10 wt% of CB to PU) with different light intensity. d) DSC curve of light-responsive shape memory materials (10 wt% of CB to PU).

Figure 3. a) The image of 3D printed film with photo-responsive shape memory behavior. b) The definition of deformation angle α . c) The effect of film thickness on the shape memory behavior of 3D printed film. d) The influence of light intensity on the shape memory behavior of 3D printed film. e) The contour map of the deformation angle increasing with both illumination time and the light intensity obtained by equation (3).

Figure 4. a) The real image of sunflower. b) Photo-triggered shape memory behavior of 3D printed sunflower from closed to opened state like the blooming of flowers. c) The different deformation of 3D printed sunflower with different illumination time under 87 mW cm^{-2} of light intensity, which were obtained every 40 s. During illumination, sunflower turned from bud to bloom. d) The infrared image of sunflower before the illumination displaying its temperature as $0.4 \text{ }^{\circ}\text{C}$. e) The infrared image of sunflower after the 280 s of illumination, showing its temperature increased to $34.4 \text{ }^{\circ}\text{C}$.

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3D printed photo-responsive devices were successfully fabricated through combining fused deposition modeling (FDM) and photo-responsive shape memory composites based on PU and carbon black. We demonstrate the shape memory behavior of these 3D printed devices was well triggered by sunshine. This development will provide tremendous opportunities for customized stimuli-responsive devices with complex geometry structure, which have potentials in soft robots, selectively pliable tools, and orthopedic surgery.

Keywords: 3D printing, shape memory devices, fused deposition modeling, photo-responsive

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