ABSTRACT: Wearable devices are now recognized as a powerful tool to collect physiological and environmental information in a smart, noninvasive, and real-time manner. Despite the rapid progress of wearable devices especially wearable electronic devices, there are still several challenges that limit their further development, for example, a complicated electrical signal acquisition and processing process to eliminate the interference from the surrounding signals, bulky power supply, inevitable e-waste, and environmental pollution. Herein, we report a 3D-printed recyclable, flexible, and wearable device for visualized UV, temperature, and sweat pH sensing. Compared with wearable electronic devices, our visualized wearable device senses environmental (UV light, ambient temperature), biophysical (skin temperature), and biochemical (sweat pH) signals via stimuli-responsive color change, which does not require complicated electronic circuit design/assembly, time-consuming data processing and additional power source. In addition, this visualized wearable device is fabricated via a 3D support bath printing technology by printing UV-, temperature-, and sweat pH-sensing inks containing photochromic, thermochromic, and pH-chromic materials, respectively, into/onto sustainable starch solution, resulting in a multi-functional, recyclable, and flexible sensing device with high reproducibility. Our results reveal that UV light intensities under sunlight (0–2500 μW/cm²), ambient, and skin temperatures (0–38 °C) as well as sweat pH (4.0–7.0) can be successfully monitored.

1. INTRODUCTION

As real-time environmental detection and in vitro healthcare monitoring, diagnostic, and therapeutic tools, wearable devices have received tremendous attention in the past two decades.1–4 Instead of cumbersome wired clinical facilities and invasive diagnostic methods, most of the wearable devices, typically in the form of small wireless electronics, can sense noninvasively a broad range of environmental signals (e.g., temperature,5 humidity,6 UV,7 etc.), biophysical signals (e.g., heart rate,8 blood pressure,9 oxygen saturation,10 skin temperature,11,12 electroencephalography,13 electrocardiography,14 electromyography,15 individual’s physical activities,16–18 etc.), and biochemical signals (sweat,19–24 tears,25,26 saliva,27,28 interstitial fluid,29 respiratory gases,30,31 metabolites,32,33 bacteria,34 and hormones35,36). Currently, wearable devices are developing toward flexibility, miniaturization, intelligence, and multi-function.36,37 Despite the remarkable progress achieved so far, wearable electronic devices still have some limitations. First of all, since wearable electronic devices are mainly based on the collection of various weak electrical signals, including current, resistance, voltage, etc., they are easy to be interfered by the surrounding environment, for example, electromagnetic wave in air and other electrical signals collected by the same device. Hence, complex electrical signal processing is often required to suppress the background signals and improve the signal-to-noise ratio.38 Second, although the sensing elements of wearable electronic devices are very small, their power supply such as an RF coil or battery occupies a relatively large area, restricting the integration of multi-function and miniaturization.39,40 Finally, wearable electronic devices are usually made of non-degradable materials, which is prone to accumulate e-waste and cause environmental pollution.41–43 Therefore, there is still an urgent need to explore new-type wearable devices based on other sensing methods that can replace in part and/or supplement the current wearable electronics.

In this paper, we propose a multi-functional, recyclable, flexible, and wearable sensing device and its relevant fabrication strategy. Particularly, herein, we report a visualized
wearable device that monitors environmental (for example, UV light, ambient temperature), biophysical (for example, skin temperature), and biochemical (for example, sweat pH) signals via a colorimetric assay rather than electrical measurement. That is, UV light intensity, ambient/skin temperature, and sweat pH are sensed and identified by the colors of UV-, temperature-, and pH-sensitive materials. Compared with wearable electronic devices, our visualized wearable device is simple and straightforward without complicated electronic circuit design/assembly, time-consuming data processing, and bulky power source. More importantly, such a visualized wearable device is fabricated via 3D support bath printing technology by printing UV-, temperature-, and sweat pH-sensing inks containing photochromic, thermochromic, and pH-chromic materials, respectively, into/onto a sustainable starch solution, which not only ensures its robust, precise, and reproducible fabrication but also endows it with excellent recyclability and flexibility (Scheme 1). We believe that this new wearable device and related fabrication method can be further extended to construct a more miniaturized yet more multifunctional visualized wearable device, which, as a low-cost and disposable wearable device, may have the potential to assist, verify, and even replace a part of the current wearable electronic devices.

2. RESULTS AND DISCUSSION

2.1. Visualized UV Sensing Via Photochromic Microcapsule. In our work, photochromic microcapsules containing spiropyrrolone (see the morphology and chemical composition of photochromic microcapsules in Figure S1 and Table S1) were selected for visualized UV sensing, owing to their reversible structural transformation between colorless spiropyrrolone and colored merocyanine upon the stimulation of UV light, as shown in Figure 1a. Figure 1b compares the UV–vis spectra of photochromic microcapsules under darkness and UV irradiation (365 nm). A new absorption peak appearing at 580 nm proves the structural conversion and color change of photochromic microcapsules after exposing to UV light. The height of this characteristic peak, or, namely, the absorption intensity at 580 nm, is found to be closely related to UV light exposure time as well as light intensity. It is clear from Figure 1c that the absorption peak at 580 nm increases dramatically when the exposure time changes from 0 to 30 s and then reaches saturation after 30 s. Similarly, this absorption peak also rises with UV light intensity in the case of the same exposure time of 30 s (Figure 1d). The rapid response time of 20 s (Figure S2) implies the high sensitivity of photochromic microcapsules to UV light. Subsequently, the selectivity of photochromic microcapsules was further examined by placing them under infrared light (IR), UV light, daylight (fluorescent lamp, D65), and sunlight. For convenience of observation, photochromic microcapsules were mixed uniformly with colorless polydimethylsiloxane (PDMS) to obtain photochromic microcapsule elastomer film (thickness: 100 μm). As can be seen in Figure 1e, the pure PDMS elastomer does not show any color no matter what kind of light sources are used. When the concentration of photochromic microcapsules in the elastomer increases from 0.2 to 2.0 wt %, the elastomer film exhibits deeper purple color under UV and sunlight while still retains white color under IR and daylight. Considering the presence of UV light in the sunlight and absence in the daylight, our data confirm the remarkable specificity and selectivity of photochromic microcapsules to UV light. Figure 1f lists the images of the photochromic microcapsule elastomer film.
films (1 wt %) under different UV light intensities. The gradually deepened purple color is in good agreement with the results obtained in Figure 1d. In addition to sensitivity and selectivity, the reversibility and stability of photochromic microcapsules for UV sensing was tested semi-quantitatively by measuring the UV−vis absorption intensities at 580 nm through repeated cycles between darkness and UV irradiation (Figure 1g). The tiny fluctuation in absorption intensities either under darkness or UV light during 10 cycles suggests the reusability of photochromic microcapsules for visualized UV sensing.

2.2. Visualized Temperature Sensing Via Thermochromic Microcapsules. Due to their widespread applications in plastics, textiles, presswork, paints, etc., thermochromic microcapsules were chosen as thermosensitive materials for visualized temperature sensing. Figure 2a illustrates their thermochromic mechanism. Generally, thermochromic microcapsules are composed of a coloring agent (thermochromic dye), a developer, and a solvent. Take red and green thermochromic microcapsules for instance, their reversible color change relies on the formation and destruction of a colored complex between the coloring agent and the developer. At low temperature where the solvent is still in its solid state, the coloring agent can transfer electrons to the developer so as to form a colored complex. Once the temperature rises to melt the solvent, the liquid solvent preferentially offers electrons to the developer and thus inhibits the electron transfer between the coloring agent and the developer. As a result, no colored complex exists and the thermochromic microcapsules become colorless. The thermochromic mechanism of the blue thermochromic microcapsule is different, i.e., the complex between the coloring agent and the developer is colorless, while the coloring agent is colored itself. In view of their high sensitivity to the environment, those materials are always encapsulated by a chemically inert resin to form microcapsules (see morphology and chemical composition of red, green, and blue thermochromic microcapsules in Figure S3 and Table S2). Figure 2b shows the photos and UV−vis spectra of red, green, and blue thermochromic microcapsules at various temperatures. Obviously, red and green thermochromic microcapsules change to white color when the temperature exceeds 4 and 24 °C, respectively, and recover their original colors when the temperature decreases below the critical values. In contrast, blue thermochromic microcapsules display white color when temperature is below 38 °C and blue color when temperature rises above 38 °C.

UV−vis spectra further confirm the color change at various temperatures. According to the complementary color law of visible white light (Figure S4), the absorption peaks at 500−540, 608, and 592 nm in the curves of red, green, and blue thermochromic microcapsules correspond to transmission light of red, green, and blue. The disappearance of absorption peaks
in the curve of red thermochromic microcapsules when the temperature rises from 4 to 24 °C proves its color change from red to white. Similarly, the absorption peaks of the green thermochromic microcapsules fade dramatically at 30 °C, while the absorption peak of the blue thermochromic microcapsules emerges at 38 °C, which is in good accordance with the results observed in photo images.

Figure 2. Visualized temperature sensing via thermochromic microcapsule: (a) schematic mechanism on visualized temperature sensing by the thermochromic microcapsule; (b) photo images and UV−vis spectra of red, green, and blue thermochromic microcapsules at various temperatures (4, 24, 30, and 38 °C); (c) photo images of hybrid thermochromic microcapsules with different red/green/blue ratios (1:1:1, 1:3:1, and 5:2:5) at various temperatures (4, 24, 30, and 38 °C) and their differences in chroma values within the CIE 1931 chromaticity coordinate; (d) optical images and infrared thermal images of thermochromic elastomer containing hybrid thermochromic microcapsules (red/green/blue = 5:2:5) at different temperatures (0−38 °C); (e) evaluation on reversibility and stability of visualized temperature sensing by measuring the wavelength of characteristic UV−vis absorption peaks of the hybrid thermochromic microcapsule at 4, 24, and 38 °C within 10 temperature cycles.

Since the color change of red, green, and blue thermochromic microcapsules occurs at distinct temperatures, their mixture at an appropriate ratio may possibly display various colors with the temperature. Figure 2c lists the photos of hybrid thermochromic microcapsules with different red/green/blue weight ratios of 1:1:1, 1:3:1, and 5:2:5 at 4, 24, 30, and 38 °C. As can be found, the hybrid thermochromic microcapsules with a ratio of 1:1:1 can change colors from
Figure 3. Visualized sweat pH sensing via methyl red: (a) molecular reaction mechanism of methyl red under acidic and neutral pH values; (b) UV–vis spectra of methyl red in ethanol, artificial sweat with pH 4.0, and artificial sweat with pH 7.0; (c) optimization of methyl red concentration for visualized sweat pH sensing; (d) color images of methyl red (0.1 wt %) under different sweat pH values (4.0, 4.5, 5.0, 5.5, 6.0, 7.0); (e) reversibility and stability of visualized sweat pH sensing via methyl red.

Figure 4. 3D-printed UV, temperature, and sweat pH sensing devices fabricated by printing sensing inks in a PDMS support bath: (a) schematic illustration on the fabrication of UV, temperature, and sweat pH sensing devices; (b) rheological properties of UV, temperature, and sweat pH sensing inks, which were prepared by blending photochromic microcapsules, thermochromic microcapsules, and methyl red with PDMS prepolymer, respectively; (c) color change of the 3D-printed UV sensing device under various UV light intensities; (d) color change of the 3D-printed temperature sensing device at various temperatures. English letters "SUCT" were prepared with different temperature sensing inks ("S": PDMS prepolymer mixed with red thermochromic microcapsules; "C": PDMS prepolymer mixed with green thermochromic microcapsules; "U": PDMS prepolymer mixed with blue thermochromic microcapsules; "T": PDMS prepolymer mixed with hybrid thermochromic microcapsules); (e) color change of the 3D-printed sweat pH sensing device exposed to artificial sweat with pH 4.0 and 7.0.
brown at 4 °C to deep green at 24 °C, white at 30 °C, and finally light blue at 38 °C. In contrast, the colors of the hybrid thermochromic microcapsules with a ratio of 1:3:1 are palm green at 4 °C, dark green at 24 °C, white at 30 °C, and light blue at 38 °C, while the hybrid thermochromic microcapsules with a ratio of 5:2:5 show red at 4 °C, light green at 24 °C, white at 30 °C, and light blue at 38 °C. Compared with the other two hybrid thermochromic microcapsules (1:1:1, 1:3:1), the hybrid thermochromic microcapsules with a ratio of 5:2:5 exhibit the most significant color difference among 4–38 °C, which is also confirmed by chroma values within the CIE 1931 chromaticity coordinate and UV–vis spectra in Figure S5.

Likewise, the thermochromic elastomer was prepared by mixing and curing the optimized hybrid thermochromic microcapsules (5:2:5) and the PDMS prepolymer. Figure 2d gives the optical and infrared thermal images of the thermochromic elastomer at different temperatures (0–38 °C). Apparently, the presence of PDMS does not affect the visualized temperature sensing performances of hybrid thermochromic microcapsules, and the response time is still less than 30 s. The infrared thermal images of the thermochromic elastomer further confirm its surface temperatures when it displays red, green, white, and blue colors. Furthermore, the reversibility and stability of thermochromic microcapsules for temperature sensing was also evaluated by measuring the wavelength of characteristic UV–vis absorption peaks of the hybrid thermochromic microcapsules at various temperatures within 10 cycles. It can be seen from Figure 2e that the wavelength of characteristic peaks shows a little deviation at 4 (~540 nm), 24 (~608 nm), and 38 °C (~592 nm) in each temperature cycle, indicating their excellent reversibility and stability for temperature sensing.

2.3. Visualized Sweat pH Sensing via Methyl Red. Methyl red, a well-known pH indicator, was used for visualized sweat pH sensing. Figure 3a illustrates its molecular reaction mechanism, which shows that methyl red exists as a protonated molecule at acidic pH and as a deprotonated molecule at neutral pH, accompanied with a color change. To explore its color change in the sweat pH range (4.0–7.0), artificial sweat solutions with pH values of 4.0 and 7.0 were prepared and methyl red-ethanol solution (0.1 wt %) was then added with a volume ratio of 1:100. Figure 3b shows the UV–vis spectra of methyl red in ethanol, artificial sweat with pH 4.0, and artificial sweat with pH 7.0. The characteristic absorption peaks at 495, 524, and 434 nm indicate their orange red, magenta, and yellow colors, respectively. Since the colors are saturated when the concentration of methyl red reaches 0.1 wt % (Figure 3c), 0.1 wt % of methyl red-ethanol solution was used for the
following tests if not specified. Figure 3d summarizes the colors of methyl red in artificial sweat with various pH values (4.0, 4.5, 5.0, 5.5, 6.0, 7.0). The one-to-one relationship between color and sweat pH proves the feasibility of visualized sweat pH sensing via methyl red. In order to assess the reversibility of sweat pH sensing, artificial sweat containing methyl red was repeatedly adjusted to either 4.0 or 7.0. As can be seen from Figure 3e, artificial sweat solutions containing methyl red exhibit red and yellow periodically as sweat pH switches between 4.0 and 7.0, implying a certain reversibility of sweat pH sensing via methyl red.

2.4. 3D-Printed UV, Temperature, and Sweat pH Sensing Devices Using PDMS as Support Materials.

After identifying the UV, temperature, and sweat pH stimuli-responsive substances, individual UV, temperature, and sweat pH sensors were first prepared by 3D support bath printing technology. Herein UV-, temperature-, and sweat pH-sensing inks were obtained by blending photochromic microcapsules, thermochromic microcapsules, and methyl red ethanol solution with the PDMS prepolymer, respectively. Figure 4a shows the fabrication procedure. For visualized UV and temperature sensors, UV-sensing and temperature-sensing inks were printed by an extrusion-based 3D printer into the PDMS support bath, and then the ink-embedded PDMS support bath was cured. For the visualized sweat pH sensor, instead of printing inside the liquid PDMS support bath, the sweat pH-sensing ink was printed onto the solidified PDMS surface. Owing to the presence of the PDMS prepolymer, the three inks demonstrate sound shear-thinning behaviors (Figure 4b) and thus acceptable printability. In addition, they also show excellent fusion with PDMS support after solidification. Figure 4c presents the printed UV sensor with a sunflower pattern. No obvious color can be observed when taking picture under the daylight. However, once exposed to low, medium, and high intensities of UV light (365 nm), the printed UV sensor can display light, medium, and dark purple colors, proving the successful construction of the visualized UV sensor via this method. Meanwhile, Figure 4d shows the as-prepared temperature sensor, where the four letters including “S”, “C”, “U”, and “T” were printed using red, green, blue, and hybrid thermochromic microcapsules (red/green/blue ratio = 5:2:5), respectively. The temperature-sensing performance of the printed letters are quite similar to the results described in Section 2.2, i.e., letter “S” is red at 4 °C and white at 24, 30, and 38 °C, letter “C” is green at 4 and 24 °C and white at 30 and 38 °C, letter “U” is white at 4, 24, and 30 °C and blue at 38 °C, letter “T” is rose red at 4 °C, green at 24 °C, white at 30 °C, and blue at 38 °C. Unfortunately, the printed sweat pH sensor does not exhibit the expected colors mentioned in Section 2.3. Specifically, it shows light pink and yellow when dropping artificial sweat (pH 4.0 and 7.0) onto its surface. This can be attributed to the low solubility of methyl red in the PDMS prepolymer and high hydrophobicity of the PDMS elastomer. As a result, only a small amount of methyl red can be mixed uniformly in PDMS and the chromogenic reaction takes a much longer time (~25 min).

2.5. Biocompatibility and Recyclability of Starch.

Although UV, temperature, and sweat pH-sensing devices can be fabricated via 3D printing using PDMS as support materials, there are still several problems to be addressed. Because the volume of PDMS changes little during the curing process, these visualized sensors are usually 1–1.6 mm thick and thus do not show excellent flexibility as often required by advanced wearable devices. The hydrophobicity of PDMS also causes long response time for sweat pH sensing (25 min). More importantly, PDMS is non-degradable and thus the visualized sensors are of poor recyclability. Cassava starch, a green natural polymer material, was tried as another alternative supporting substance for the visualized wearable devices. Since traditional starch films are very brittle and fragile, several cross-linkers, such as epichlorohydrin, formaldehyde, phosphorus oxychloride, etc., were used to improve their mechanical properties. In our study, sodium trimetaphosphate (STMP) was selected as the cross-linker due to its authorization as a green and safe food additive by Food and Drug Administration (FDA), Figure 5a gives the cross-linking reaction equation between STMP and starch, which improves not only the mechanical strength of starch but also its stability in water solution. In addition, glycerol was also added into the starch solution as a plasticizer to further enhance its flexibility because glycerol can form hydrogen bonds with starch, weaken the strong hydrogen bonds between internal starch molecules, and thus increase the mobility of starch molecule chain segments. The parameters including the reaction time and the concentrations of STMP and glycerol were optimized as 1.5 h, 0.5 wt %, and 2 v/v %, according to the transparency and mechanical properties of the modified starch films (Figures S6 and S7). Figure 5b shows the photos and transmissivity in the visible light range of as-prepared starch films using optimal parameters. As can be observed, the modified starch film are very thin, flexible, and transparent (up to T = 88.6% at 550 nm), which can attach to the human skin easily. The cytocompatibility of starch film was also characterized by live/dead staining of fibroblasts (L929 cells) after seeding these cells onto the starch film surface and culturing for 1, 3, and 5 days (Figure 5c). No significant difference can be found between the control group (culture on well plate) and the experimental group (culture with starch film), suggesting the good cytocompatibility of modified starch film. On the other hand, the degradation of starch films was investigated in tap water at 37 °C using a shaker. Figure 5d shows the photos of starch film after soaking in tap water for various times. Note that a blue dye was mixed into starch film for the convenience of observation. The starch film starts to swell after soaking for 30 min, doubled at 20 h, degrades on day 2, and finally disappears (fully degrades) on day 10, indicative of its excellent recyclability and environmental friendliness. Despite the rapid degradation in water, the modified starch film is quite stable in air (relative humidity: 50%), as illustrated in Figure S8.

2.6. Visualized UV, Temperature, and Sweat pH Sensing Via 3D-Printed Recyclable, Flexible, and Wearable Devices.

Visualized UV, temperature, and sweat pH sensors using recyclable starch as a supporting substance were also fabricated via 3D support bath printing technology. Similar to PDMS-based sensing inks, starch-based UV-, temperature-, and sweat pH-sensing inks were prepared by blending photochromic microcapsules, hybrid thermochromic microcapsules (red/green/blue ratio = 5:2:5), and methyl red ethanol solution with starch solution. Figure S9 shows the rheological properties of starch and starch-based sensing inks. Our results reveal that good printability can be achieved using 8 wt % of starch solution for sensing ink preparation. Different from individual sensing devices, an integrated flexible wearable device for multifunctional sensing (UV, temperature, and sweat pH) was constructed by printing UV-, temperature-, and sweat pH-sensing inks in turn into/onto the same starch support
bath and slowly heating the whole materials system (sensing inks and support bath) to remove water. To better collect the sweat and accelerate the sweat pH sensing process, a thin filter paper was covered onto the surface of printed sweat pH-sensing inks (Figure S10). It should be pointed out that distinct patterns, i.e., letter “U” for the UV-sensing ink, letter “T” for the temperature-sensing ink, and a circle shape for the sweat pH-sensing ink, were printed to distinguish the UV, temperature, and sweat pH sensors. As a consequence, a thin starch film (100−150 μm) containing three sensing materials can be obtained as a recyclable, flexible, and wearable device for visualized UV, temperature, and sweat pH sensing.

Figure 6a shows the UV sensing performance of the as-prepared multifunctional wearable device under sunlight over time. As can be found, the letter “U” displays purple color quickly (response speed <20 s) with various brightness when the times are 8:00 am, 10:00 am, 12:30 pm, 14:30 pm, and 17:30 pm. According to the relationship between purple brightness and UV light intensity shown in Figure 1f, the UV light intensities are 300, 500, 900, 750, and 65 μW/cm². For comparison, a commercial UV irradiation meter was used to measure the UV light intensity at the same time. The small difference between the two methods proves the feasibility of our wearable device to monitor UV light intensity outdoor.

The temperature sensing performance of the wearable device was subsequently evaluated, and the results are shown in Figure 6b. When the flexible wearable devices are used to detect low temperature (putting an ice pack onto the flexible wearable device), medium temperature (air-conditioned room), and high temperature (skin temperature), the letter “T” exhibits red, green, and gray white with a response speed of ca. 30 s. Also, the temperature can be identified as 5.8, 23.3, and 33.8 °C by colorimetry using the data shown in Figure 2d, which are very close to the values (6.3, 24.4, and 34.0 °C) measured by the commercial infrared thermometer. Next, the sweat pH sensing was conducted by attaching the flexible wearable devices onto the necks of five male and five female volunteers who vigorously exercised for 20 min and sweated a lot (Figure 6c). The sweat collected by the thin filter paper (<150 μL) makes the methyl red in the printed circle become red in a very short response time (2 min), and the sweat pH can be read from Figure 3d. The improved response time of sweat pH sensing (2 min) using the starch substrate compared to the PDMS substrate (25 min) can be attributed to the faster penetration of sweat through the filter paper and starch. Interestingly, our results further reveal that the sweat pH values of males (4.2−4.8) are lower than those of females (4.8−5.4), implying the difference in the physiological environment between males and females. Finally, the anti-interference capability of the three sensing modes in the same wearable device is demonstrated in Movie S1. Obviously, UV, temperature, and sweat pH sensing in our device do not show interference with each other and no false positive signals are observed, indicative of their high reliability and specificity.

In addition, no obvious leakage of colorimetric reagents is observed during the testing process. This can be attributed to the following reasons: First, colorimetric reagents for visualized UV and temperature sensing are encapsulated in photochromic
or thermochromic microcapsules. These microcapsules are then 3D-printed into starch supporting bath. Their microscale size can prevent the leakage of microcapsules after solidification of the starch supporting bath. Second, methyl red, for sweat pH sensing, is mixed with starch paste and thus adhered well to the surface of the starch substrate. The presence of filter paper can further absorb and reduce leakage of methyl red to a large extent. Future digitization of this multifunctional visualized wearable device can be performed with the aid of common portable instruments (portable scanner, camera, and smart phone) to realize more accurate sensing.

3. CONCLUSIONS

In summary, we describe in this paper a 3D-printed recyclable, flexible, and wearable device for visualized UV, temperature, and sweat pH sensing. Specifically, we first investigate the feasibility of photochromic microcapsules, thermochromic microcapsules, and methyl red as UV-, temperature-, and pH-sensitive materials. Our results reveal that photochromic microcapsules, thermochromic microcapsules, and methyl red show good sensitivity, stability, and reversibility to UV light, temperature, and sweat pH, respectively. Then, individual visualized UV, temperature, and sweat pH sensing devices are prepared by 3D printing technology using PDMS as support bath material. It is found that the presence of PDMS does not affect the performance of UV and temperature sensing but prolongs the response time of sweat pH sensing mainly due to the low solubility of methyl red in the PDMS prepolymer and high hydrophobicity of PDMS. To overcome the problems associated with PDMS such as hydrophobicity and non-degradability, cassava starch, a green natural polymer material, is used as a recyclable and flexible substance after cross-linking and plasticification. Excellent biocompatibility and recyclability of the modified starch are proven by live/dead staining of L929 cells and degradation test in tap water. Finally, an integrated recyclable, flexible, and wearable device for visualized UV, temperature, and sweat pH sensing is fabricated via 3D printing technology using starch as support bath material. Our data confirm that UV light intensities under sunlight, ambient, and skin temperature as well as female and male volunteers' sweat pH can be successfully monitored. It should also be noted that although the starch-based substrate is recyclable, the colorimetric reagents including photochromic microcapsules, thermochromic microcapsules, and methyl red are not usually recognized as green materials. Green visualized reagents are still needed in the future. We believe that the new visualized wearable device and its fabrication strategy can be further extended to other wearable devices with more functional sensing ability, which offers a promising solution to the problems of the current wearable electronic devices.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. Polydimethylsiloxane (PDMS) (Sylgard 184) was purchased from Dow Corning Company (USA). Cassava starch (moisture ≤13 %) was obtained from Foodstuff and Technology Investment Corporation (Vietnam). Sodium trimetaphosphate (purity: 99.5%) and glycerin (purity ≥99.0%) were bought from Macklin and Guangzhou Chemical Reagent Company (China), respectively. Methyl red (purity 99.5%) was purchased from Guangzhou Chemical Reagent Factory (China). Thermochromic and photochromic microcapsules were obtained from New Prismatic Enterprise Co., Ltd. (China) and Thousand Color Change Co., Ltd. (China), respectively.

4.2. Printing UV-, Temperature- and Sweat pH-Sensing Inks in PDMS Support Bath. The UV-sensing ink was prepared by adding 1 wt % of photochromic microcapsules into a mixture of the PDMS base and curing agent (10:1, w/w). The temperature-sensing ink was obtained by first blending red, green, and blue thermochromic microcapsules at a weight ratio of 5:2:5 and then adding 200 mg of mixed thermochromic microcapsules into 10 g of PDMS prepolymer. The sweat pH-sensing ink was made by mixing 1 wt % of methyl red-ethanol solution with the same quality of PDMS prepolymer. All the three sensing inks were degassed and stored in a 4 °C refrigerator for future use. Later, UV-sensing and temperature-sensing inks were printed by an extrusion-based 3D printer (3D Bio-Architect TB Mini, Regenovo, China) into a PDMS support bath (a mixture of PDMS base and curing agent at a weight ratio of 10:1), and then the ink-embedded PDMS support bath was cured at 120 °C for 20 min. Instead of printing inks inside the liquid PDMS support bath like UV-sensing and temperature-sensing inks, the sweat pH-sensing ink was printed onto the solidified PDMS surface.

4.3. Preparation and Characterization of Transparent Starch Film. A total of 10 g of cassava starch, 0.05 g of sodium trimetaphosphate, and 2 g of glycerin were added successively into 100 mL of deionized water and stirred at 30 r/min. After gelatinizing at 85 °C for 1.5 h, 25 mL of starch paste was poured into a Petri dish and placed in an oven at 40 °C for 6 h to obtain the transparent starch film. The biocompatibility of the starch film was evaluated as follows: The starch films were sterilized by soaking in 75% of alcohol and exposing to UV light for 24 h. After rinsing with PBS buffer, L929 cells at a density of 3 × 10^4 /mL were seeded onto the starch films and cultured for 1, 3, and 5 days in DMEM (Gibco, Thermo Fisher Scientific, USA) with 10% fetal bovine serum and 1% penicillin–streptomycin solution in a CO₂ incubator at 37 °C. Cell viability was tested by live/dead staining via a calcine AM/ethidium homodimer live/dead assay (Life Technologies, NY). Specifically, 100 µL of PBS solution was added to wash it twice and the buffer containing 0.1 v/v% of calcine AM and 0.3 v/v% PI was then added and incubated for 30 min at 37 °C. The stained cells were characterized by an inverted fluorescence microscope (ZEISS Axio Observer 7). Meanwhile, the degradation of starch films was performed in tap water at 37 °C using a shaker.

4.4. Fabrication of Multifunctional Sensors by Printing Sensing Inks in Starch Support Bath. Similar to the preparation of UV-, temperature-, and sweat pH-sensing inks in the PDMS substrate, photochromic microcapsules, thermochromic microcapsules, and methyl red were individually added into gelatinized starch solution and stirred for 1.5 h at 85 °C to obtain UV-, temperature-, and sweat pH-sensing inks. Thereafter, UV-sensing and temperature-sensing inks were printed into 25 mL of starch support bath and dried at 40 °C for 6 h in an oven. Finally, sweat pH-sensing ink was printed onto the dried starch film so as to obtain a starch film with UV-, temperature-, and sweat pH-sensing functions.

4.5. Characterization of Material Properties and Sensing Performance. The morphologies of the photochromic microcapsules and thermochromic microcapsules were observed with a scanning electron microscope (SEM, NanoSEM 430, Nova). The UV–vis spectra of thermochromic
microcapsules, photochromic microcapsules, and methyl red indicator composites were collected with a UV–vis spectrophotometer (TU1901, Persee, Beijing). The rheological properties of sensing inks were probed via a rheometer (RST-SST, Brookfield). Mechanical properties of starch films (W × L: 0.5 cm × 3 cm) were tested using a WE-30 universal testing machine (Instron 5967, USA) in tension mode.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00128.

SEM image of photochromic microcapsules; chemical composition of photochromic microcapsules; response time of photochromic microcapsules to UV light; SEM images of thermochromic microcapsules; chemical composition of thermochromic microcapsules; complimentary color law of visible white light; UV–vis spectra of the hybrid thermochromic microcapsules with a weight ratio of 5:2:5 at various temperatures; optimization of reaction time for starch modification; optimization of sodium trimetaphosphate (STMP) and glycerol concentrations for starch modification; stability of modified starch in the air; rheological properties of starch-based sensing inks; and sweat pH sensor using starch as supporting substance (PDF)

Anti-interference capability of the three sensing modes in the same wearable device (MP4)

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Notes
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