Hydrochromic CsPbBr$_3$-KBr Microcrystals for Flexible Anti-Counterfeiting and Wearable Self-Powered Biomechanical Monitoring

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**ABSTRACT**

Metal-halide perovskites (MHPs) featured with excellent photoelectronic properties and low-temperature solution processability are emerging as desired candidates for next-generation wearable and portable electronics. However, irreversible emission properties quenching of MHPs in the presence of water has severely impeded their versatile applications. Here, we present a facile water–ethanol assisted co-precipitation strategy for cost-effective and eco-friendly fabrication of hydrochromic smart luminescent CsPbBr$_3$-KBr microcrystals (CPB-K). Interestingly, the as-prepared CPB-K can achieve reversible transition between luminescent and non-luminescent state upon the water removal/exposure owing to the dissolution/recrystallization of luminescent CsPbBr$_3$ nanocrystals with the help of KBr salts. The coating of polydimethylsiloxane (PDMS) effectively prevents the destruction of CPB-K and maintains its green emission upon moisture. Further, by leveraging the hydrochromic CPB-K and water-resistant CPB-K/PDMS characteristic synergistically realize multiple encryption effects of information, and the hidden information can be clearly identified upon moisture decrystallization. Because of electrical and dielectric properties of MHPs, a flexible triboelectric nanogenerator (TENG) made from CPB-K/PDMS film as friction layer has been constructed with maximum open-circuit voltage of 43.4 V (loading CPB-K of 20 wt%), about 1.8 times that of the pristine PDMS-based TENG. Additionally, we demonstrate a self-powered wearable sensor based on CPB-K/PDMS TENG for real-time biomechanical monitoring with electrical signals. This work provides an eco-friendly fabrication approach for perovskite-based smart luminescent materials, which further opens up the possibility to expand their diverse applications in wearable electronics.

1. Introduction

Wearable electronics, which makes possible the flexibility, multifunctionality and integratability of our daily electronic devices, is an emerging technology owing to the rapid development of diverse fields, including big data, artificial intelligence and Internet of Things [1–6]. In general, a complete wearable system requires flexible sensors [7–9], electronic displays [10,11], field-effect transistors [12,13], and electrical power source circuits [14,15] as basic units, while power supply unit provides basic security to maintain the durable operation of the multifunctional devices. In this regard, various energy-harvesting devices, such as solar cells [14,16], biofuel cells [17,18], thermal gradient [19–21], and triboelectric/piezoelectric devices [22–27], have been rapidly developed to harvest energy from surroundings or directly generate electricity to support the operation of the device. Among these devices, the triboelectric nanogenerators (TENGs) based on a coupled effect of electrostatic induction and triboelectricity have drawn enormous attentions due to characteristic advantages, such as wide availability of low-frequent energy harvesting, easy fabrication and cost-effectiveness [28,29]. As a result, TENG-based energy-harvesting devices...
have been demonstrated to be widely employed as wearable powering, self-powered sensing, and personal healthcare monitoring [22,30]. Moreover, to improve efficiency of TENG, various multifunctional-materials-based fillers, such as ZnO, lead zirconate titanate (PZT) and piezoelectric perovskite of BaTiO$_3$ have been developed [31–33]. However, complexity, high growth temperature, and cost-intensive process represent major challenges in fabrication and growing of such inorganic nanomaterials. Also, rigid and brittle nature of such materials always results in specific deformations in a minimal range [34]. Consequently, tremendous efforts have been committed to develop the potential materials easily to be prepared, inexpensive and multifunctional to construct high performance TENGs [35–39].

Recent newly emerging metal-halide perovskites, with formula of A$_{3}$PbX$_3$ (where A = Cs$^+$/CH$_3$NH$_3$$^+$/CH(NH$_2$)$_2$$^+$, X = Cl, Br, I), have been widely employed for numerous optoelectronic applications, such as light-emitting diodes (LEDs), displays and lasers due to their narrow spectral emission, tunable bandgap, high defect tolerance, and facile solution processing [40–44]. Considering the remarkable dielectric and electrical properties of MHPs, several perovskite-based materials have been introduced into the TENGs, paving a new way for their development. For example, Zhu et al. reported the triboelectric effect of MAPbI$_3$ perovskite and obtained an open-circuit voltage of 8 V and a short-circuit current of 200 pA [45]. Further, a dynamic metal/perovskite Schottky junction-based direct-current generator has been experimentally proved serving MA$^+$/FA$^-$/PbI$_2$/SnO$_2$/Si as friction material [46]. To obtain robust perovskite-based TENG, Tang et al. introduced relatively stable CsPbBr$_3$ perovskite as triboelectric material with tunable morphologies, space charge polarization, triboelectric charge density and dielectric properties [47,48]. In addition, perovskite decorated polymers, such as CsPbBr$_3$/PVDF, FAPbBr$_3$/PDMS and CsPbBr$_3$/NOA63, as piezoelectric layer have been explored to improve the output of piezoelectric nanogenerator [34,49,50]. The hybrid triboelectric and piezoelectric nanogenerator based on Cs$_6$Bi$_3$Br$_{16}$ perovskite/PVDF nanofiber enhanced the performance of TENGs, which possessed great electrical output (400 V, 1.63 μA cm$^{-2}$, and 2.34 W m$^{-2}$) [51]. These results demonstrated the perovskite-based materials can effectively enhance the output performance of TENG, whereas few reports pay attention to other functions of perovskite-based materials. Nevertheless, the requirement of flexible electronics with multi-functional characteristics is very urgent for different applying scenarios in the future. Therefore, it is highly desirable to explore new functions of perovskite-based materials, which is conducive to the development of multifunctional sensor devices.

Smart luminescent materials that can response to external stimuli (such as mechanical force, heat, gas, light, and moisture) exhibited adjustable optical properties (emission color or intensity) [52–54]. In particular, hydrochromic materials which can response to moisture attract growing interests owing to their low cost, easy detection and fast response [54]. Unfortunately, the developments on hydrochromic property of perovskite-based materials are still impeded, which can be ascribed to their poor stability against water, resulting in the irreversible transformation in PL emission [55–57]. In a striking work, Yu et al. proposed a space-confined strategy to obtain reversibly hydrochromic CsPbBr$_3$ nanocrystals by loading them into porous matrices [54]. Recently, Ma et al. developed a porous framework of super-hydrophobic polydivinylbenzene (PDB) to absorb Cs$_x$PbBr$_{3-x}$ QDs and the obtained composite achieved water-induced photoluminescence enhancement and dehydration responsiveness [58]. Meanwhile, the formation of CsPbBr$_3$ NCs induced by water has been demonstrated in borophosphate-based glass, and the glass powders gradually changed their photoluminescence from blue to green (478–525 nm) [59]. Unfortunately, the anti-counterfeiting method based solely on the corresponding optical properties of perovskite may not protect films effectively and is easy to clone. PL materials with multiple encryption characteristics have been considered a effective strategy to solve this problem [60], as it is more difficult for forgers to replicate these behaviors but smart hydrochromic CsPbBr$_3$ perovskite materials with multiple encryption characteristics have not been reported yet. Additionally, a facile, eco-friendly and cost-effective preparation process is essential for both multifunctional device applications and smart luminescent materials. Water is the most eco-friendly, sustainable and low-cost solvent, while the aqueous synthesis route has not been considered as applicable for smart luminescent perovskite owing to their instability in water and the poor solubility of PbX$_2$ in water [61].

Here, we present a fast, low-cost and eco-friendly water–ethanol assisted co-precipitation strategy, using water and ethanol as green solvents, to synthesize hydrochromic smart luminescent CPB-K composite. It can achieve reversible hydrochromic conversion by exposure/removal of water. Combining with PDMS (Fig. S1), the hydrochromic CPB-K and waterproof CPB-K/PDMS enable to achieve the multiple encryption effects of information and decryption by moisture. Additionally, the as-obtained flexible CPN-K/PDMS film also can be employed for TENGs device, and the output performance of CPB-K/PDMS-based TENGs improves about 1.8 times than PDMS-based TENGs. The device also hold excellent operation stability and can maintain its performance during 15,000 cycles of mechanical stress. Furthermore, a self-powered sensor is demonstrated for real-time monitoring different parts of human movement. Therefore, this work not only offers a new finding and an eco-friendly fabrication approach for perovskite-based smart luminescent materials, but also may open a way for perovskite materials based multifunctional sensing applications.

2. Experimental Section

2.1. Materials

Material details are listed in Supplementary data.

2.2. Preparation of CPB-K

Typically, the KBr salt was completely dissolved in water (3 ~ 4.2 mol/L, 15 mL) under stirring, to form a KBr aqueous solution. Then solid PbBr$_2$ (1.5 mmol) was dissolved to the KBr aqueous solution by stirring and ultrasound treatment for one hour, and then added CsBr (1.5 mmol) to obtain an aqueous solution of halogen precursor. Finally, the supernatant was quickly dropped into a beaker of ethanol solvent under stirring for 24 h. The as-prepared samples were directly centrifuged or dried to obtain solid-state CPB-K microcrystals.

2.3. Fabrication of CPB-K/PDMS thin films and anti-counterfeiting patterns

First, the PDMS precursor solution was obtained by mixing the A and B components with weight ratio of 10: 1. Then CPB-K composite of different mass fractions was added into the well mixed PDMS solution to form CPB-K/PDMS inks, followed by constantly stirring for 1 h at 800 r min$^{-1}$. The obtained uniform CPB-K/PDMS paste was directly blade-cast onto the flexible PET substrate on the glass plate and sequentially changed the corresponding height of the scraper to 50, 100, 250 and 500 μm to obtain a flat film. Finally, the CPB-K/PDMS film was cured at 80 °C for three hours for procuring. The custom-made printed patterns were covered on flexible PET substrate for anti-counterfeiting patterns. The inks based on CPB-K and CPB-K/PDMS were dropped on respective area of the template, and then inks were printed on the PET under the pressure exerted by the scraper. After cured at 80 °C for three hours, the anti-counterfeiting patterns were obtained by removing the template.

2.4. Fabrication of flexible TENG and sensor

The well-mixed CPB-K/PDMS ink was directly coated on flexible electrode (including copper film electrode and ITO/PET) through blade-coated method, and then cured at 80 °C for three hours. Then, leaded a wire from the electrode, and a flexible TENG was obtained. The TENG
was directly fixed to the different parts of the body by adhesive tape and a wearable sensor was obtained.

2.5. Characterizations

Characterization details are listed in Supplementary data.

3. Results and discussion

Fig. 1a schematically illustrates the co-precipitation method for preparation of CPB-K composite at room temperature. Here, we synthesized CPB-K in water/ethanol system based on Equations (1) and (2):

\[
PbBr_2 + 4KBr \rightarrow [PbBr_6]^{4-} + 4K^+ \quad (1)
\]

\[
CsBr + [PbBr_6]^{4-} + 4K^+ \xrightarrow{H_2O} 4KBr + CsPbBr_3 \quad (2)
\]

First, PbBr\(_2\) reacts with KBr aqueous solution to form \([PbBr_6]^{4-}\) complex; and the added CsBr can be dissolved in aqueous solution of \(K^+\) and \([PbBr_6]^{4-}\) owing to its high solubility in water (123 g in 100 mL \(H_2O\) at 25 °C) [62]. Therefore, we obtained the ionic state of salts (Cs\(^+\), \([PbBr_6]^{4-}\), Br\(^-\) and K\(^+\)) in transparent aqueous solution. Then ethanol was employed to precipitate these soluble inorganic salts by feat of their solubility difference in water and ethanol. As illustrated in Fig. 1a, the precursors were quickly added to ethanol under stirring, and the solution instantaneously changed its color to yellow with bright green photoluminescence (PL) under UV lamp (365 nm) and PLQY up to 53.04 % in ethanol (Fig. S2), indicating the formation of CPB-K composite. More details about the synthesis process were presented in Experimental Section. We further compared it with other different solvent systems (DMF/ethanol and HBr/ethanol) and reveals KBr not only helps dissolve PbBr\(_2\) in \(H_2O\) but also acts as matrices to protect CsPbBr\(_3\) NCs with bright green photoluminescence (Fig. S3). Moreover, the co-precipitation method is easy to scale up (Fig. 1a), which does not require high temperature, inert gas, toxic solvents and other redundant post-processing process. Therefore, this method is in line with advocacy of green chemistry and provides a new options for large-scale and cost-effective production for perovskite-based materials. Fig. 1b and 1c presented the scanning electron microscope (SEM) images of CPB-K with a relatively rectangular shape and average diameter of 1.4 µm (Fig. S4). The basically similar shape and size of composites indicate that they have shape retention and sufficient compactness, which can be used as fluorescent inks (inset in Fig. 1a and S5). Besides, the CPB-K composites have relatively frizzy edges because of the effect originated from the water of surrounding environment. To verify the incorporation of CsPbBr\(_3\) NCs in KBr matrices, we studied the chemical composition of the CPB-K through energy dispersive spectroscopy (EDS) measurements. The element of Cs, Pb, Br, and K were dispersed on the particles, indicating the CsPbBr\(_3\) NCs incorporation in KBr matrices (Fig. 1e). Transmission electron microscopy (TEM) measurement was performed to further verify the existence of CsPbBr\(_3\) NCs. Fig. 1d displays numerous NCs distributed inside KBr particle. It should be noted that KBr salts are high volatility and easy to damage under an electron beam [63]. Thus the particles of perovskite NCs were gradually exposed when the electron beam irradiation as depicted in Fig. S6. The existence of shadows was the KBr salts after electron beam irradiation, implying the perovskite NCs were buried in KBr. The high-resolution TEM image shows the crystal lattice of 0.29 nm for corresponding to the (2 2 0) crystal plane of CsPbBr\(_3\) (Fig. S6d). It is well known that perovskite NCs are so vulnerable that high temperature and polar solvents can accelerate degradation of their structure, resulting in serious PL quenching [64]. Here, the bright fluorescence of CPB-K was highly stable in ethanol/water system, and the corresponding PL intensity did not show obvious decrease after storage in ethanol four months owing to the protection of KBr salts (Fig. S7). The comparison of the ethanol stability with other reported perovskite-based materials were listed in Table S1. The PLQY of our products in this work is not particularly high, only 53.04 %, thus it is expected that the high PLQY of products will be obtained in our subsequent follow-up report. In order to obtain solid-state smart luminescent materials, the ethanol and aqueous solvents were directly

Fig. 1. (a) Synthesis procedure diagram of green-emissive CPB-K composite at room temperature. (b, c) SEM, and (d) TEM images of CPB-K composite. (e) EDX elemental mappings for Cs, Pb, Br and K, the scale bars are 800 nm. (f) Digital photographs of as-prepared CPB-K/PDMS film under 365 nm UV light with various deformations. (g) Light transmittance spectra of PDMS and CPB-K/PDMS film, corresponding photographs as depicted in inset.
removed by volatilization (Fig. S8), which is an eco-friendly and low-cost route. Moreover, the obtained solid-state samples have excellent heat resistance owing to free of organic ligands [65]. As shown in Fig. S9, the solid-state samples deposited on the glass sheet can keep their bright green emission after being heated at different temperatures (20 °C ~ 160 °C, the gradient interval is 20 °C). All these results demonstrated that our CPB-K composite has the more superior thermostolerance and ethanol resistance to maintain its excellent luminescent properties. In general, incorporating CsPbBr$_3$ NCs into a polymer matrix, physically blending may sacrifice their optical and corresponding mechanical properties owing to poor compatibility and aggregation of CsPbBr$_3$ NCs, while the dynamic and ionic lattice band structure of CsPbBr$_3$ NCs utilized by KBr in this work may improve compatibility with various resins [66]. Then, PDMS was chosen to serve as an encapsulation matrix for CPB-K to prepare flexible emissive layers owing to its high transparency, flexibility and durability [67]. The optical photographs of the CPB-K/PDMS film in the relaxed, crimp, fold, stretched, twist and restore states under 365 nm UV light (Fig. 1f) clearly displays the highly luminescent and superior flexibility of the CPB-K/PDMS film. Light transmittance spectra of PDMS and CPB-K/PDMS film on PET substrate were presented in Fig. 1g, exhibiting excellent visible light transmittance.

X-ray diffraction (XRD) measurements were performed to analyze the phase structure of as-prepared CPB-K, PDMS and CPB-K decorated PDMS film (Fig. 2a). The main diffraction peaks of CPB-K composite at 2θ = 23.3°, 27.0°, 38.5° and 47.7° matched well with the (1 1 1), (2 0 0), (2 2 0) and (2 2 2) planes of cubic KBr (PDF#36-1471). For CPB-K decorated PDMS film, three characteristics peaks at 2θ = 23.3°, 27.0° and 38.5° can be ascribed to the plane (1 1 1), (2 0 0) and (2 2 0) of KBr, while pristine PDMS film showed a broad steamed bread peak and no distinct peak belongs to KBr and CsPbBr$_3$ crystals. It should be noted that a few other diffraction peaks can be observed in XRD pattern of CPB-K, owing to very little concentration of PbBr$_2$ and CsBr precursors. The XRD pattern of pure CsPbBr$_3$ without addition of KBr and CPK-K (Fig. 2a and S10) illustrated the diffraction peaks at 15.2°, 21.5° and 30.7°, which can be assigned to (1 0 0), (1 1 0) and (2 0 0) plane of CsPbBr$_3$ (PDF#18-0364), respectively [68,69]. Unfortunately, when KBr was not added, the product did not exhibit obvious photoluminescence (Fig. S10). Raman spectrum of the CPB-K (Fig. S11) shows slight deviation (located at 76 and 130 cm$^{-1}$) compared with CsPbBr$_3$ crystals (located at 70 and 125 cm$^{-1}$), which may result from surrounding environment or influence of other metal halides structures [70]. Fig. 2b depicts the optical absorption and corresponding PL spectra of CPB-K composite (the inset shows its photograph under 365 nm UV light). A sharp absorption slope from about 534 nm can be observed, and the estimated optical band gap is about 2.32 eV by extrapolating the linear fit of the Tauc plot to the energy axis (Fig. S12), in agreement with the value of CsPbBr$_3$ of previous reports [71]. A sharp PL peak at 522 nm...
with a narrow FWHM of only 21 nm is also in line with CsPbBr$_3$ NCs reported before, also demonstrating the bright green emission of CPB-K resulting from CsPbBr$_3$ NCs [54]. Furthermore, X-ray photoelectron spectroscopy (XPS) determined corresponding surface element and the valence states of K, Cs, Pb, and Br in CPB-K (Fig. 2c-2f). Those binding energy peaks at 737.6 and 723.7 eV (Fig. 2d) can be attributed to the Cs 3d$_{3/2}$ and Cs 3d$_{5/2}$ states. The binding energy peaks located in 137.8 and 142.6 eV (Fig. 2e), originate from spin-orbit splitting of Pb 4f$_{7/2}$ and 4f$_{5/2}$, which are in agreement with the XPS signals of Pb$^{2+}$ in the CPbBr$_3$ perovskite. The peaks of Br at 67.9 and 68.9 eV can be attributed to the Cs$_{3d_{5/2}}$ and Cs$_{3d_{3/2}}$ states. These results are in line with the value of CsPbBr$_3$ NCs in previous reports [72,73]. Corresponding crystal structure schematic diagram of CsPbBr$_3$ perovskite was illustrated in Fig. 2g. With 25 wt% of CPB-K loading, the Fourier-transform infrared (FTIR) spectroscopy of PDMS film (Fig. 2h) did not show obvious deviation of Si-CH$_3$, Si-O-Si, and Si-(CH$_3$)$_2$ peaks [74] except for their intensity increase, indicating crosslinking between PDMS and CPB-K. Moreover, we note that the CPB-K composite is uniformly dispersed in the PDMS sol without settling, implies that the as-prepared film hold great uniformity with bright green emission (inset in Fig. 2i). In addition, The PL intensity increased with the addition of CPB-K in PDMS film, indicating tunable optical properties of CPB-K/PDMS film via different content doping (Fig. 2i).

Hydrochromic materials, as one kind of smart luminescent materials, are responsive to moisture and water to change their luminescent intensity or color, which have gradually attracted enormous attentions owing to their low cost, fast response and easy operation [54]. To date, no experimental reports about the hydrochromic characteristic based on CPB-K composite materials have been reported yet. Fig. 3a displays the schematic illustration of corresponding reversible transformation process between green-emissive CPB-K composite and non-luminescent ionic liquid according to Equations (1) and (2). To further understand this point, the fluorescence changes of CPB-K based films under 365 UV light at various humidity conditions (RH = 40 %~80 %) are presented in Fig. S13, indicating the excellent water stability of CPB-K based films at lower humidity. Because of strong solubility of CsBr in water [62], and CsPbBr$_3$ itself is ionic nature, so, during 90 % moisture treatment, stripping of CsBr will occur, which forces the decomposition of CsPbBr$_3$.
resulting in the PL quenching of CPB-K based film. Since the ionic state provides enough precursors, once the water or moisture was evaporated, the CPB-K composite will regenerate and the corresponding film will recover its green emission as displayed in Fig. S14. We have also conducted the additional experiments about its performance degradation process more than 15 times of exposure/removal of water cycle, which exhibits relatively long cycle lifetime. The transformation process of CPB-K solid-state composite under UV light is also shown in Fig. 3a. Considering PDMS is chemically orthogonal to CPB-K composite, the coated PDMS provides excellent protection for CPB-K composite and prevents it dissolve in water, thus still maintains its green emission. In other words, the CPB-K composite achieves reversible off/on of green emission state between moisture and drying, while CPB-K/PDMS still keeps its original green emission state even with moisture treatment. The corresponding process is similar to the encryption and decryption process of anti-counterfeiting patterns (Fig. 3b). Anyone can see the information under 365 nm UV light, but this is not true, and only the insider who holds the key (moisture) can unlock it and encrypt the hidden information again. For further understand this point, we designed the encrypted anti-counterfeiting patterns employing CPB-K composite and CPB-K/PDMS as the inks. Fig. 3c depicts photographs of unencrypted patterns made from CPB-K/PDMS. It retained the original and bright green emission pattern even after moisture treatment. In Fig. 3d, the “small fish” was encrypted using CPB-K composite rather than CPB-K/PDMS ink. By decrypting the information with moisture, the green-emissive CPB-K composite was converted into non-luminescent state, and the fish disappears. Subsequently, drying treatment can restore the “small fish” again by generating CPB-K composite, thus making the decoding process nearly trackless. Similarly, a leaf of rose with CPB-K ink presented the green emission under 365 nm UV light,

![Fig. 4. (a) Schematic structure of single-electrode mode TENG. (b) Working mechanism of CPB-K/PDMS-based TENG device. (c) Simulation of electrical potential distribution of the TENG by COMSOL software. (d-f) Open-circuit voltage, short-circuit current, and transferred charge amount of TENG with various CPB-K content under same test condition. (g-i) Open-circuit voltage, short-circuit current, and transferred charge amount for the TENG with different frequencies (1–5 Hz) under same test condition. (j) Durability testing of TENG for continuous 15,000 cycles at 2 Hz. (k) Magnification of regions marked in (j).]
and its green emission can disappear after moisture decryption. Therefore, utilizing the synergy of CPB-K and CPB-K/PDMS fluorescent inks, the unpredictable information encryption and anti-counterfeiting can be effectively achieved.

We further expanded the types of ink by using PVB, PVP and alcohol-soluble acrylic resin (Fig. 3f), and the solvent is green and low-cost ethanol, indicating the excellent compatibility of CPB-K composite. The CPB-K composite can also be employed as a green phosphor in blue phosphor. A white emitting device was achieved, which provides an effective approach to applying CPB-K composite prepared by water ethanol co-precipitation in LEDs. Fig. 5g provides the electroluminescence (EL) spectra of the corresponding device driven at 20 mA current, which consists of three distinguishable emission bands of blue, green and red. The working white-light LED exhibits bright white emission (inset of Fig. 5g) with the correlated color temperature(CCT) 4953 K and the Commission Internationale de L’Eclairage (CIE) color coordinate (0.34, 0.33) at operating current of 20 mA (Fig. 3i). Moreover, the color gamut areas of the obtained LED using CPB NCs-K solid-state composite was calculated to be approximately 123.4 % of the National Television Standards Committee (NTSC), higher than the Cd-NC LEDs (NTSC 104 %) [75]. Fig. 3i presents the EL spectra of WLED under different currents ranging from 20 to 120 mA. All these results demonstrate that our CPB-K composite ink has great potential in for anti-counterfeiting and light applications.

After designing material with excellent optical properties, flexibility and stability, we need to focus on its application for wearable electronic devices. Based on the as-prepared CPB-K/PDMS elastomers, a single-electrode mode TENG was developed. Fig. 4a displays a structural schematic diagram of TENG, composed of PDMS film and a flexible copper sheet as the outer electrode. The electrical signals of various thicknesses of the CPB-K/PDMS film are shown in Fig. S15. Moreover, the PL intensity of CPB-K/PDMS increases with film thickness owing to more luminaries in the membrane (Fig. S16). The mover part, composed of various active materials (Fig. S17) with a flexible substrate, was grounded through wire. The corresponding work mechanism of operation of the TENG was illustrated in Fig. 4b. In the initial state, the active material of Cu film is completely contacted with the CPB-K/PDMS under an external mechanical force. The surface charges are induced due to contact electrification, with the equivalent number of positive and negative triboelectric charges distributed at the active material and CPB-K/PDMS surfaces, respectively (Fig. 4b and 4i). After that, when the mover part gradually separates from the outer CPB-K/PDMS, positive charges will be instantly induced on the Cu electrode. The electrical potential difference between the Cu electrode and the ground will force the free charges to flow to the ground, thus giving an output current (Fig. 4b and 4ii). Next, when the mover part moves far enough, a new balanced state occurs and thus circuit no longer generates corresponding charge movement (Fig. 4b and 4iii). Finally, when the mover part attaches the CPB-K/PDMS again, the electrons will move back from the ground to the Cu electrode owing to balanced charges (Fig. 4b and 4iv). The above process of TENG keeps its circulating and the corresponding alternating current will appear through continuous separation movement and contact. Through COMSOL, we observed the electric potential distribution during contact and separation state between CPB-K/PDMS film and Cu electrode film based on a finite-element theoretical model, thus further understanding the principle of the power generation process of one cycle (Fig. 4c and S18). The introduction of perovskite-based materials into TENGs has been demonstrated to improve their output performance, and the presence of some intrinsic defect in perovskite may play a key role as these defects can be employed as electron trapping acceptors to maintain more negative charges [51]. In addition, the non-centrosymmetrical crystal structure for [PbBr₆]₄⁻ octahedral offers orientational disorder and polarization effect which can enhance the triboelectric output [47]. Therefore, the CPB-K doping concentration under the same mechanical force was investigated to optimize the TENG output performance (Fig. 4d-4f). A doping concentration of 20 % in mass fraction of CPB-K generated the highest electrical outputs with an open-circuit voltage of 43.4 V, a short-circuit current of 955 nA, and a charge transfer amount of 17.2 nC when contacting with a Cu film, larger than the un-doped PDMS (24.2 V, 440 nA, and 8.8 nC). The value of open-circuit voltage of TENG at CPB-K loading of 20 wt% exhibits nearly 1.8 times higher than PDMS-based TENG. The open-circuit voltage, short-circuit current, and short-circuit charge transfer were also measured under the various frequencies (1 ~ 5 Hz). These values of open-circuit voltage and short-circuit charge transfer are nearly stable, reaching to 42 V and 15 nC, respectively. Meanwhile, a higher impact frequency induces a higher short-circuit current. The obtained short-circuit current can approach 900 nA at the frequency of 5 Hz. In addition, the corresponding stability of the TENG was tested by continuously tapping device. As illustrated in Fig. 4j, the open-circuit voltage remains almost 42 V after 15 000 cycles without obvious degradation in electrical output, indicating great mechanical robustness and reliability. Furthermore, the TENG exhibited excellent long-term stability, presented in Fig. S19.

Generally, physiological signal characteristics of different parts of human body are different, they will also produce unique characteristics under different external stimuli. These corresponding signals can be collected to detect human motion [22]. The obvious sensitivity changes from 2.10 to 0.48 V/N with various loading forces, and the sensor is more sensitive in relative low-pressure state (Fig. S20). Therefore, the obtained TENG sensor was attached to various parts of the human body (Fig. 5) with the adhesive tape, and corresponding voltages signals were collected in real-time. By sticking the device on the neck, throat-related activities can also be reflected. For example, the output voltage can arise 1.2 V as drinking and 0.6 V as speaking “Beijing” (Fig. 5a), which can further distinguish the state of drinking or speaking according to a corresponding characteristic peak of voltage signal (Fig. S21). The muscle movement of the human arm can also be monitored (Fig. 5b). When the arm is forced, the sensor voltage increase to 2.8 ~ 3.7 V under different forces, and when the arm is relaxed, the output voltage returns to zero, which is expected to be used for motion analysis in the process of athletes’ movement. Fig. 5c presents the output voltage of the sensors on a wrist of tester. When the wrist is bent forward from the vertical position, the sensor is stretched and in contact with the skin. Meanwhile, the sensor is compressed and corresponding output voltage increase from 0 to 7.5 V (blue line), while the wrist return to the vertical position, the sensor returns its initial state and voltage output decrease to 0 V. When the wrist is bent backward from the vertical position, the voltage output increases from 0 to 9.8 V. Without halting at vertical position, the voltage output increase from 0 to 20.2 V. These results can be ascribed in the larger contact pressure between the sensors and skin, indicating potential application for the sensors to distinguish the different movement forms of the same part [76]. Furthermore, we directly pressed the sensor with one finger, two fingers and palm, which showed that the output signal of the sensor also increases with increased contact area (Fig. 5d and S22). The sensor with different areas was tested (Fig. S23) under the same force, and the results are consistent with the above results. The sensor can also distinguish different motion angles. For example, output voltage gradually increases when the finger is bent with increased bending angles (from 30°, 60° to 90° as shown in Fig. 5e), indicating potential application for human–machine interaction. For monitoring of belly movement during normal breathing, the output signal displayed a uniform signal output (Fig. 5f). By sticking the sensor on the knee, ankle and forehead, the corresponding voltage output were dissimilar owing to their different physiological signal characteristics (Fig. 5g-S5). Even at the same angle, the output signal of leg rising and driving movement was different (Fig. S24), which is expected to set up a more personalized human–computer interaction system. Fig. S25 presented the motion state of foot by bundling a sensor on ankle with two ways containing the foot up and down, which indicates the up or down.
movement can be judged according to the output electrical signal. Furthermore, real-time output signals of the sensor under the forefeet demonstrates the movement state of walking or running. Therefore, the self-powered TENG sensor can be used to detect daily and clinical body motion for potential applications of human health monitoring or intelligent robotics.

4. Conclusion

In summary, we have demonstrated an easy scale-up method for facile, eco-friendly and cost-effective fabrication of hydrochromic CPB-K microcrystalline employing water and ethanol as green solvents. Our as-prepared composite shows an average particle size of 1.4 µm and a PLQY of 53.04 %, which can be applied as a green conversion hub for white LEDs. Moreover, the CPB-K is also compatible with various polymers such as PDMS, PVP, PVB and alcohol-soluble acrylic resin, exhibiting potential application in fluorescent ink. Specially, the hydrochromic CPB-K successfully realized the reversible transition luminescent on/off state employing water as the external stimuli. The synergy effect between hydrochromic CPB-K and water-resistant CPB-K/PDMS anti-counterfeiting inks enables to realization of the encryption and decryption of information upon moisture treatment. Based on the electrical and dielectric properties of CPB-K, we further developed a single-electrode mode flexible TENG employing CPB-K/PDMS as dielectric layer. The open-circuit voltage of TENG at CPB-K loading of 20 wt% exhibits nearly 1.8 times higher than PDMS-based TENG. As a proof of concept application of wearable electronics, a self-powered flexible sensor based on CPB-K/PDMS TENG for real-time sensing of different parts of human movement is demonstrated. We believe that such smart luminescent perovskite-based materials with simple fabrication will expend for a wide array of wearable electronic devices that have been obstructed by existing approaches.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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