

Stable Ultrathin Perovskite/Polyvinylidene Fluoride Composite Films for Imperceptible Multi-Color Fluorescent Anti-Counterfeiting Labels

Junlu Sun, Qilin Hua, Mengqi Zhao, Lin Dong,* Yu Chang, Wenqiang Wu, Jing Li, Qiushuo Chen, Jianguo Xi, Weiguo Hu, Caofeng Pan,* and Chongxin Shan*

As an essential part of information security in the Internet of Things (IoT), fluorescent labels possess a principal portion of anti-counterfeiting due to its easy fabrication, low cost, and high yield. Here an ultrathin, stable, and patterned multi-color fluorescent label with perovskite/polyvinylidene fluoride composite film is presented, which registers a resolution of 56.4 dpi and almost maintains its original fluorescent intensity after being immersed in water for 120 h. The variable color of fluorescent labels will improve the anti-counterfeiting dimensions for the information security due to precise halogen constitutions. The imperceptible fluorescent labels are typically with a thickness of 1.2 μm and a weight of 1.2 mg. They can be conformally adhered on the arbitrary curved substrate as the intelligent multi-color fluorescent anti-counterfeiting labels for IoT applications.

techniques have been proposed and developed.^[10–14] Among them, the fluorescent label may be more prominent with its easy fabrication, low cost, and high yield. Diverse fluorescent materials have been introduced to fabricate fluorescent labels, including organic quantum dots (QDs),^[15–17] inorganic QDs,^[18,19] and rare-earth compounds.^[20–22] Owing to their exotic photo-physical characteristics: tunable bandgap,^[23] high visible-light absorption,^[24] and high quantum yield,^[25,26] perovskite materials have been the promising candidate for optoelectronic devices, which could help the fluorescent label with its value in the anti-counterfeiting of information security.

1. Introduction

Information security is of vital importance in Internet of Things (IoT),^[1–3] where anti-counterfeiting is widely used in oceans of applications ranging over economic activities, military operations, and individuals' daily lives.^[4–9] Various anti-counterfeiting

However, the poor stability of perovskite materials within the ambient conditions, especially under humidity, remains the obstacle to their widespread applications. Several strategies have been put forward to improve the stability, such as composition modulation,^[27] surface passivation,^[28] and matrix encapsulation.^[29,30] Thereinto, the matrix encapsulation with compact polymer chain could effectively shelter perovskite materials from water molecular. Zhou and co-workers have enhanced the humidity stability and thermal stability of perovskite composite film by embedding perovskite nanocrystals (NCs) in polymer matrix.^[30] Meantime, the photoluminescence (PL) was also enhanced due to the in-situ formation of perovskite NCs in polymer matrix.^[31] Hydrophobic polyvinylidene fluoride (PVDF) was introduced to improve the stability of perovskite fluorescent labels in water, saline, ethanol, dichloromethane and so on. After 120 h in water, the fabricated fluorescent labels still maintained the almost original fluorescent intensity, which exhibited its high stability.

In addition, the fabrication of well-patterned perovskite arrays remains to be challenging, which sets limits in the applications of those flexible and ultrathin fluorescent labels. Generally, patterned perovskite arrays could be synthesized via anodized aluminum (AAO) template,^[32] epitaxial growth,^[33] and chemical vapor deposition,^[34,35] which are not suitable for perovskite/PVDF composite films due to the decomposition under severe environment such as organic solvent or high temperature in the fabrication process. Therefore, a feasible fabrication protocol for patterned perovskite arrays of flexible and ultrathin fluorescent labels is most expected.

J. Sun, Prof. L. Dong, Y. Chang, Prof. C. Shan
Henan Key Laboratory of Diamond Optoelectronic Materials
and Devices

Key Laboratory of Materials Physics
Ministry of Education
School of Physics and Microelectronics
Zhengzhou University
Zhengzhou 450001, P. R. China

E-mail: ldong@zzu.edu.cn; cxshan@zzu.edu.cn

J. Sun, Dr. Q. Hua, M. Zhao, W. Wu, J. Li, Q. Chen, Dr. J. Xi, Prof. W. Hu,
Prof. C. Pan

CAS Center for Excellence in Nanoscience, Beijing Key Laboratory
of Micro-nano Energy and Sensor

Beijing Institute of Nanoenergy and Nanosystems
Chinese Academy of Sciences
Beijing 100083, P. R. China
E-mail: cfpan@binn.cas.cn

Dr. Q. Hua, J. Li, Prof. W. Hu, Prof. C. Pan
School of Nanoscience and Technology
University of Chinese Academy of Sciences
Beijing 100049, P. R. China

 The ORCID identification number(s) for the author(s) of this article
can be found under <https://doi.org/10.1002/admt.202100229>.

DOI: 10.1002/admt.202100229

In this work, a hydrophilic-hydrophobic mosaic modified approach is introduced to obtain patterned arrays with a resolution of 56.4 dpi. The patterned fluorescent labels greatly increase the complexity of anti-counterfeiting technology. The colors of fluorescent labels could change with various halogen constitutions, which would increase the anti-counterfeiting dimensions for the information security in IoT applications. According to the practical applications in IoT, the imperceptible multi-color fluorescent labels are obtained with a thickness of 1.2 μm and a weight of 1.2 mg, which possess conformality, imperceptibility, easy integration, and other excellent characteristics. These labels may act as anti-counterfeiting labels and authentication terminals of IoT and artificial intelligence (AI).

2. Results and Discussion

Figure 1a schematically illustrates the fabrication process of the perovskite/PVDF composite films. First, the precursor solution of perovskite/PVDF was dropped on the substrate (e.g., glass or plastic) pre-treated under oxygen plasma and then the composite film was achieved by spin-coating. The film was then cured in a vacuum oven at room temperature for 5 min to expedite the volatilization of DMF. The inserted optical images in Figure 1a depict the film color at the corresponding step of fabrication process. By tuning the halogen constitution of perovskite, three primary colors (i.e., blue, green, and red) were successfully achieved under the illumination of 365-nm UV light, as shown in the insets of Figure 1b. The perovskite/PVDF composite films with three primary colors are further characterized through PL spectra, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). As shown in Figure 1b, the perovskite/PVDF films exhibit typical intrinsic

near band edge emission, and the optical images of the corresponding samples rendering three primary colors are clearly illustrated. The characteristic diffraction peaks of about 14.9° , 30.2° , 33.7° , and broad peak at 20.7° were observed in the XRD patterns of perovskite/PVDF composite films. The broad peak is attributed to the overlap of (110) and (200) crystal face of β -phase PVDF, while the other peaks are for perovskite materials with different halogen constitutions. Figure 1d shows the Fourier transform infrared (FTIR) spectra of perovskite/PVDF composite films with the three primary colors. The characteristic peaks at 510 and 839 cm^{-1} were due to the absorption band of β -phase PVDF.

Commonly, anti-counterfeiting technology requires diverse colors to increase the anti-counterfeiting dimensions for the information security in IoT applications. Impressively, by varying the halogen constitution, the perovskite/PVDF composite films can deliver abundant colors ranging from blue to red under UV-light (365 nm), as shown in Figure 2a. The corresponding PLs span from 400 to 720 nm, covering the full visible-light region, as shown in Figure 2b. The Commission International de l'Eclairage (CIE) coordinate diagram of perovskite/PVDF composite films with various halogen constitutions was calculated from their PL spectra to demonstrate the tunable multi-color characteristics, which is illustrated in Figure 2c.

In addition to the tunable colors, patterning is of much importance to greatly increase the complexity of anti-counterfeiting technology. In general, the patterns can be fabricated by the conventional microfabrication processes, such as UV lithography and lift-off. However, most organic solvents adopted in the UV lithography and lift-off process (such as photoresist, developing solution, and acetone) will seriously destroy the fluorescence of the perovskite/PVDF composite film. Although some groups developed novel methods which were used to take

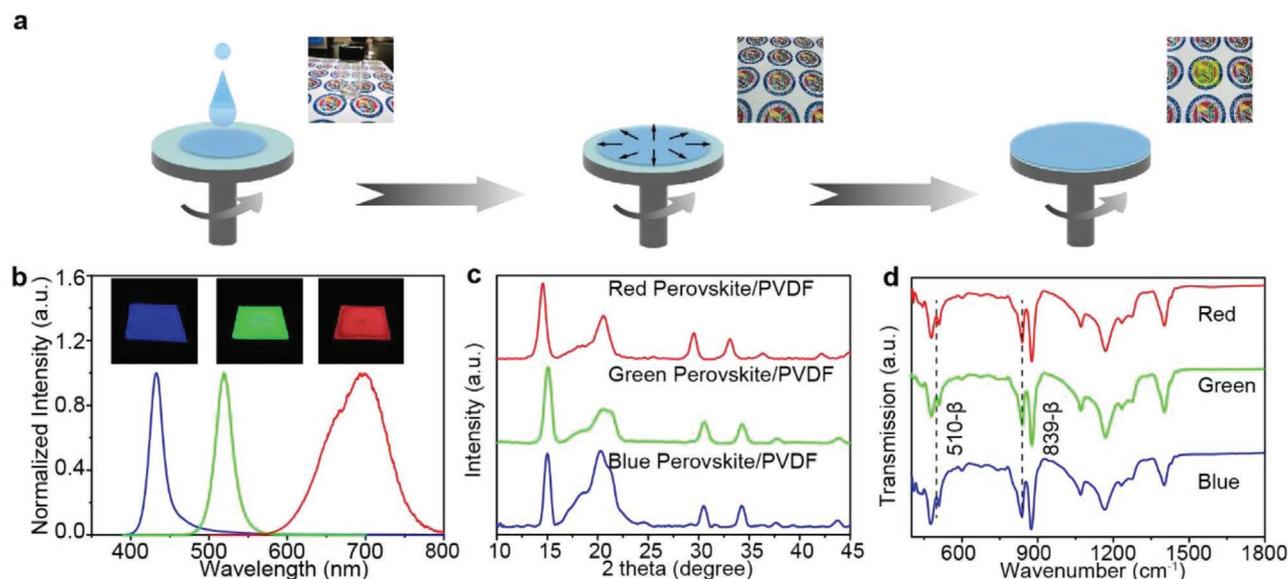


Figure 1. Fabrication process and characterization of the perovskite/PVDF composite films. a) Schematic illustration of the spin-coated perovskite/PVDF composite films. b) Photoluminescence (PL) spectra of the perovskite/PVDF composite films with three primary colors (i.e., blue, green, and red; the corresponding halogen compositions are $\text{Cl}_{2.5}\text{Br}_{0.5}$, Br_3 , $\text{Br}_{1.5}$, respectively.) through varying halogen constitution under the illumination of UV light. The insets show the corresponding fluorescence images of blue, green, and red emission. c) X-ray diffraction (XRD) patterns and d) Fourier transform infrared (FTIR) spectra of the perovskite/PVDF films with three primary colors.

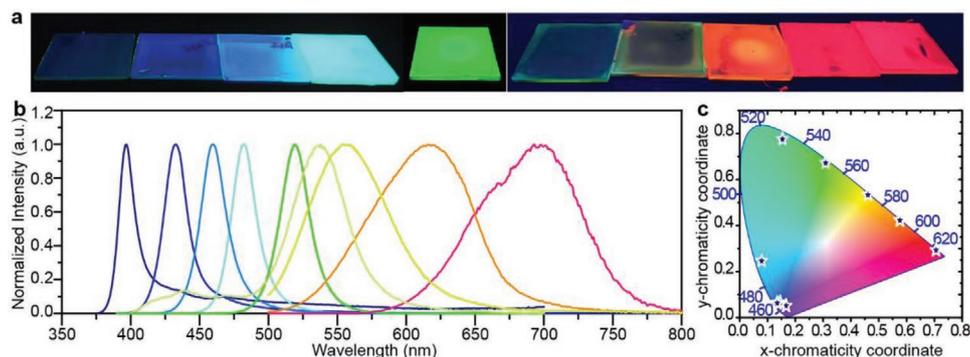


Figure 2. Multi-color demonstration and characterizations of the tunable perovskite/PVDF composite films with varying halogen constitutions. a) Optical fluorescence images of the multi-color perovskite/PVDF composite films under UV lamp (365 nm) (the corresponding halogen compositions (X_3) are Cl_3 , $\text{Cl}_{2.5}\text{Br}_{0.5}$, Cl_2Br , ClBr_2 , Br_3 , $\text{Br}_{2.5}\text{I}_{0.5}$, Br_2I , $\text{Br}_{1.5}\text{I}_{1.5}$, BrI_2 , $\text{Br}_{0.5}\text{I}_{2.5}$, respectively). b, c) the PL spectra and the corresponding CIE chromaticity diagram of multi-color perovskite/PVDF composite films.

the place of high-temperature methods for patterned perovskite arrays,^[36] these, unfortunately, are not suitable for device fabrication on polymeric flexible substrates. To obtain the high-resolution fluorescent labels, a hydrophilic-hydrophobic treatment method is introduced to fabricate the patterned perovskite/PVDF composite film. The schematic structure of the patterned perovskite/PVDF array is illustrated in **Figure 3a**, which consists of (octadecyl) trichlorosilane (OTS) treated hydrophobic areas and the other patterned hydrophilic areas covered by the perovskite/PVDF arrays. First, the specific patterns could be pre-fabricated on the substrate with the UV lithography. After modification, the patterned substrate was treated with OTS

to get hydrophobic areas, where the affinity of the perovskite/PVDF precursor solution was abruptly decreased. And then, via the lift-off technique, the substrate with hydrophilic-hydrophobic patterns was successfully prepared. Finally, the perovskite/PVDF precursor solution was spin-coated on the prepared substrate. The precursor solution just stays on the hydrophilic patterns. And the patterned perovskite/PVDF arrays could be formed after the thermal treatment in a vacuum oven. The detailed process steps are schematically illustrated in **Figure 3b** and **Figure S1**, Supporting Information. Specifically, the hydrophilic-hydrophobic treatment method could be available for various substrates, including rigid and flexible configurations.

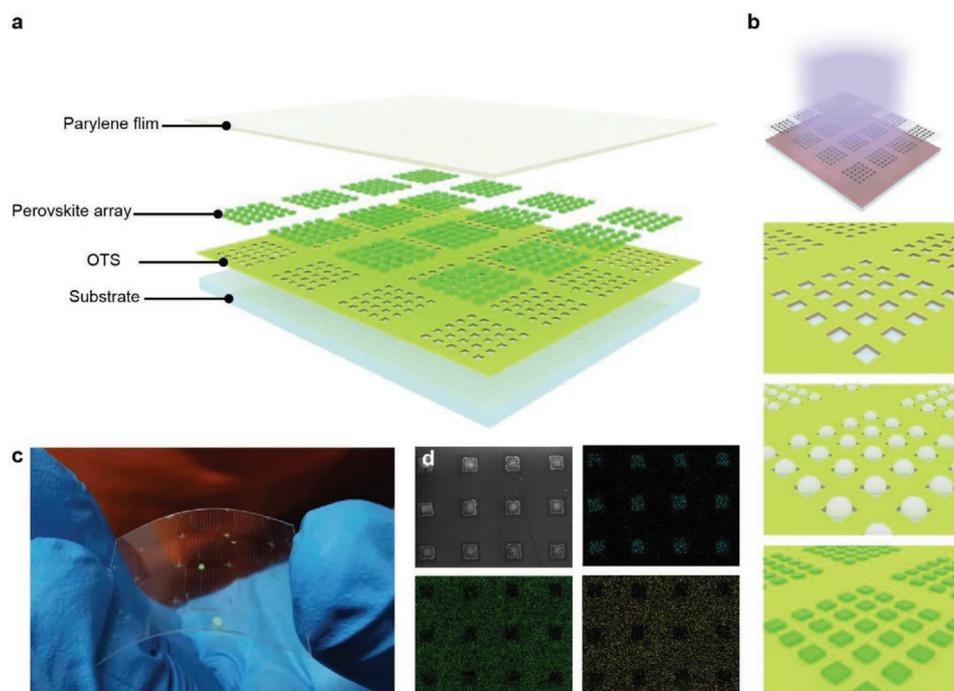


Figure 3. Flexible patterning method of the perovskite/PVDF composite films. a) Schematic structure of the flexible patterned perovskite/PVDF composite films. b) Schematic fabrication process. c) Photograph of flexible patterned perovskite/PVDF composite films. d) Scanning electron microscopy (SEM) images of the patterned perovskite/PVDF composite film, and the corresponding energy dispersive spectra (EDS) mapping of elements of F, Si, O.

Moreover, as-patterned perovskite/PVDF arrays on the flexible substrate are demonstrated in Figure 3c. The morphology of the patterned perovskite/PVDF arrays was characterized by a scanning electron microscopy (SEM). The corresponding elemental distribution mappings (including F, Si, and O) of the patterned perovskite/PVDF arrays were conducted by an energy dispersive spectrometer (EDS). The hydrophilic areas were clearly distinguished by the mapping of element fluorine from PVDF, while the hydrophobic areas by elements Si and O from the OTS layer did. Furthermore, the fluorescent colors of the perovskite/PVDF patterns can be adjusted by varying the halogen contents, as shown in Figure S2a–c, Supporting Information. And the arbitrary complex patterns with tunable multi-colors (e.g., RGB) are capable to be easily fabricated (Figure S3, Supporting Information), which are the vital point of fluorescent labels for anti-counterfeit applications. The multi-color perovskite/PVDF arrays with various patterns were obtained and illustrated in the Figure S3, Supporting Information. Hereinafter, we take the devices with green fluorescence for an example to further investigate the key characteristics of the imperceptible fluorescent anti-counterfeiting labels.

For the fluorescent anti-counterfeiting labels, uniformity and stability are both essential attributes for the patterns and their pixels in the long term. **Figure 4a** shows the optical image of the patterned perovskite/PVDF arrays with highly uniformity and stability. The enlarged detail of each pixel from perovskite/PVDF arrays is illustrated in **Figure 4b**, indicating a resolution

of 56.4 dpi. The patterned arrays have the consistent fluorescence intensity under UV light (365 nm), and each pixel displays excellent fluorescence characteristics. Five typical pixels marked in a green rectangle (**Figure 4b**) are enlarged and illustrated in **Figure 4c** together with their uniform fluorescence intensity. From the full-width at half-maximum (FWHM) of the fluorescence pixels, the resolution of the patterned fluorescent labels is about 100 μm .

As is well known, perovskite materials are very sensitive to ambient humidity. Water molecules can easily penetrate the perovskite structure to form hydrate structure, which would lead to the deprotonation of perovskites. To verify the stability under humidity environment, the patterned perovskite/PVDF arrays were immersed in water for a period. As shown in **Figure 4d**, the device exhibits no fluorescence degradations in water after more than 120 hours. The optical images and fluorescence intensities of the patterned fluorescent label in water were recorded every 12 h (**Figure S3**, Supporting Information). Two representative images (at the initial and end of 120 h) and fluorescence intensities of five representative pixels every 12 h are illustrated and plotted in **Figure 4d**. After 120 h, every pixel of the arrays is clearly distinguished and fluorescence intensities could almost maintain identical to that of the initial one. Due to the instruction of the hydrophobic PVDF, the stability of fluorescence labels have been improved in water or other commonly-used solutions (e.g., saline, ethanol, and dichloromethane in **Figure S5**, Supporting Information).

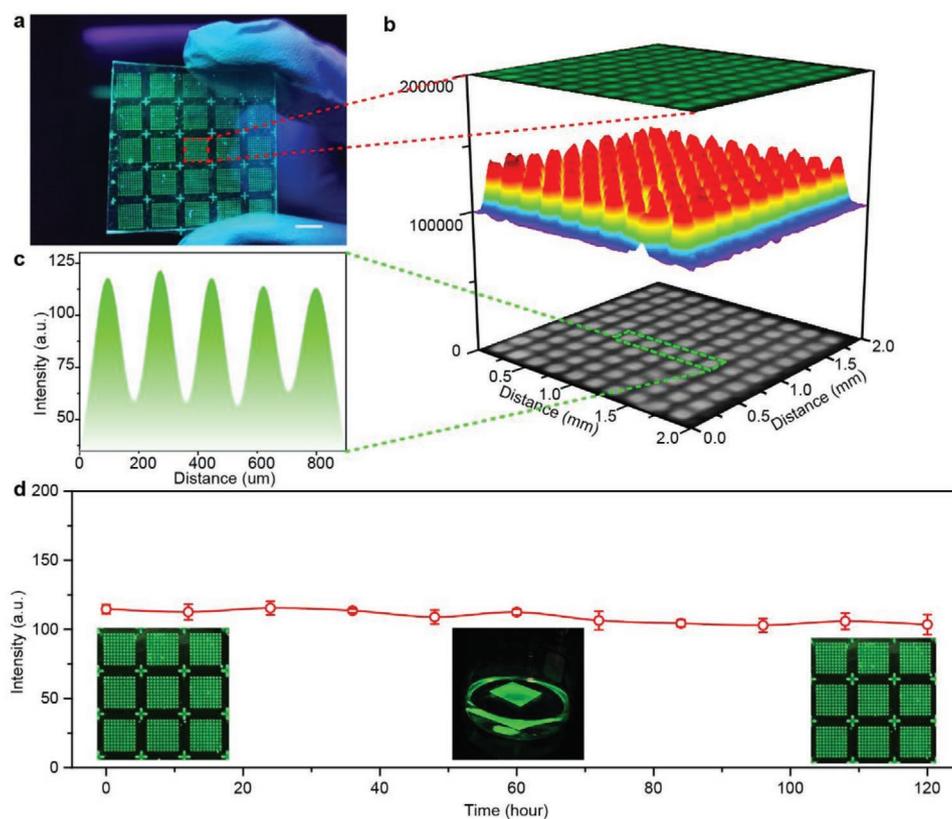


Figure 4. Uniformity and stability of the perovskite/PVDF composite film. a) Optical image of the perovskite/PVDF composite film with square patterned arrays. b) The detailed uniformity presentation of each pixel of the patterned fluorescent label. c) The fluorescent intensities of five typical pixels marked in a green dashed rectangle in (b). d) Stability of the patterned perovskite/PVDF composite film in water over 120 h.

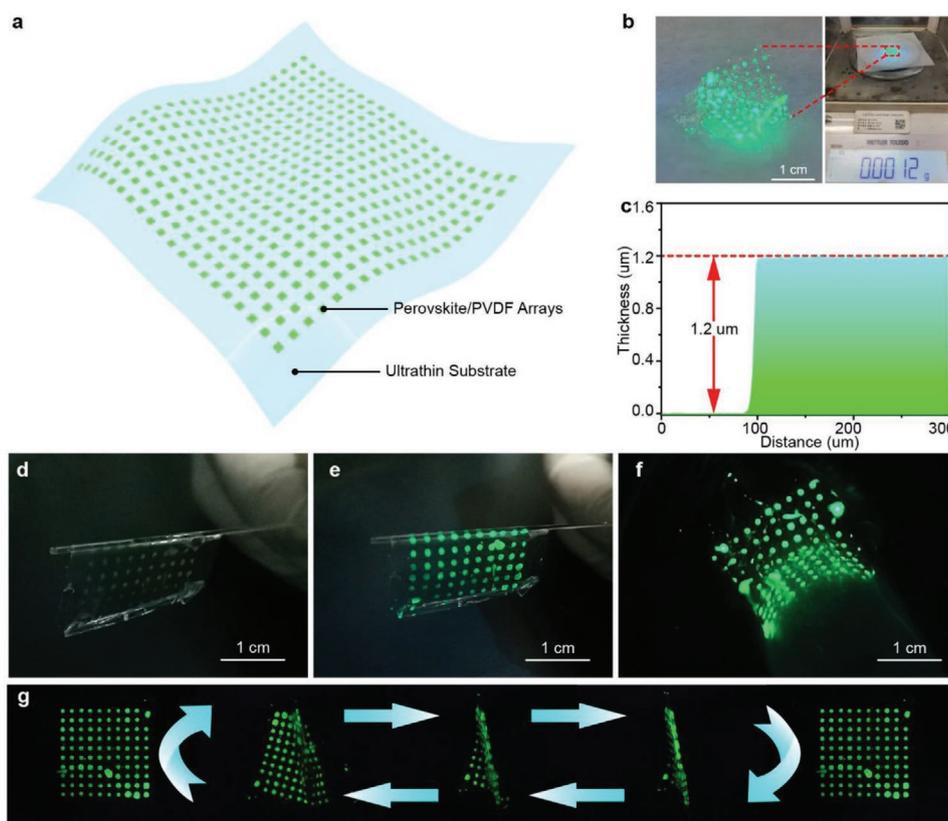


Figure 5. Illustration and characterization of the ultrathin fluorescent labels. a) 3D schematic illustration of ultrathin fluorescent label. b,c) The light-weight and ultrathin configurations of the crumpled ultrathin fluorescent label under UV-light (365 nm). d,e) Optical images of ultrathin fluorescence label hung up by a glass fiber with 1 mm diameter and under UV light (365 nm). f) Conformal characteristics of fluorescent labels, which could be adhered on arbitrary curved substrate. g) The reversible process of ultrathin fluorescent label crimping.

To meet the practical requirements in the IoT, the imperceptible features (i.e., ultrathin, ultra-lightweight, and transparent) are deployed on the fluorescence labels with the optimal process. **Figure 5a** schematically shows the 3D illustration of an imperceptible fluorescence label, which consists of a ultrathin parylene-C substrate and patterned perovskite/PVDF arrays. The impressive characteristics of ultra-lightweight (1.2 mg) and ultrathin (1.2 μm) are shown in Figure 5b and c, respectively. Additionally, the transparency can be observed in Figure 5d. Under the illumination of UV light (365 nm), the green fluorescence pattern arrays are obviously demonstrated. Moreover, the labels could be conformed and attached to any arbitrary complex curve surfaces (Figure 5d–g; Figure S6, Supporting Information), due to the ultrathin and ultra-light-weight properties, which are very suitable for anti-counterfeiting. As shown in Figure 5d, an imperceptible fluorescence label is hung up by a glass fiber with a diameter of 1 mm. The dangling label shows the excellent fluorescent phenomenon under UV light (365 nm). And it still works even for the case being crumpled like a sheet of paper (Figure 5b). To indicate the highly reversibility and stability, the imperceptible fluorescence label is hung out from the surface of water by the glass fiber, and reversibly put back in water. Interestingly, the green fluorescence does not show any obvious degradation during the testing procedures for many times. And

the detailed procedures are shown in Figure S6 and Movie S1, Supporting Information.

3. Conclusion

The imperceptible multi-color fluorescent anti-counterfeiting labels based on ultrathin, stable, and tunable perovskite/PVDF composite films have been successfully fabricated through the hydrophilic-hydrophobic treatment method. The imperceptible label of 1.2 μm in thickness and 1.2 mg in weight was demonstrated with a resolution of 56.4 dpi. More impressively, it showed a prominent stability under humidity in water for over 120 h, which breaks through the dilemma of perovskite materials in moisture ambient. Due to conformality, the ultrathin fluorescence labels are easy to be adhered on arbitrary curved surface and peeled off easily, which could be a potential candidate for anti-counterfeiting applications in the IoT. The diverse colors and various patterns of the fluorescence labels could help with the increase in dimensions and complexity of anti-counterfeiting for the information security. Such imperceptible multi-color fluorescent labels with ultrathin, stable, and tunable features would be an effective and efficient way for anti-counterfeiting and authentication terminals of IoT and AI.

4. Experimental Section

Materials: Lead chloride (PbCl₂, 99.9%), lead (II) bromide (PbBr₂, 99.9%), lead (II) iodide (PbI₂, 99.9%), methylammonium chloride (MACl, 99.9%), methylammonium chloride (MABr, 99.9%), and methylammonium iodide (MAI, 99.9%) were obtained from Xi'an Polymer Light Technology Corp. *N,N*-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.5%), (octadecyl) trichlorosilane (OTS), and poly(vinylidene fluoride) (PVDF, $M_w \approx 400\,000$) were purchased from Sigma-Aldrich.

Fabrication of Perovskite/PVDF Composite Films: PbX₂ and MAX (X: Cl, Br, I) (1 mmol) were mixed in the solution of DMF/DMSO (1 mL) to form solution A. PVDF (1 g) was dissolved in DMF (5 mL) to form solution B. solution A (0.1 mL) was mixed in solution B (5 mL) to form precursor solution. The precursor solution was spin-coated on substrate and then transferred into a vacuum oven to rapidly remove the DMF at the low pressure for 5 min. Finally, the multi-color perovskite/PVDF films were fabricated through adjusting the composition of halogen.

Fabrication of Ultrathin Fluorescent Labels: In order to obtain ultrathin substrate, parylene-C was deposited on Si wafer by thermal evaporation. First, about 50 nm SiO₂ film was deposited on parylene-C/Si through radio frequency (RF) magnetron sputtering (PVD75 Kurt J. Lesker) and then treated by O₂ plasma to obtain a hydrophilic substrate. Second, the SiO₂ film surface was patterned by UV lithography technique (MA6 SUSS). Third, as-processed substrate was treated by (octadecyl) trichlorosilane (OTS) and lift-off process to obtain patterned arrays with hydrophilic surface. Finally, the precursor solution of perovskite/PVDF was deposited on the hydrophilic surface to form the PPFTs. To achieve multi-color perovskite/PVDF patterns, precursor solutions with variant composition were used to develop multiple colors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.S., Q.H., and M.Z. contributed equally to this work. The authors thank for the support of the National Natural Science Foundation of China (11674290, U1704138, 11974317, and 61904012), Beijing City Committee of Science and Technology (Z171100002017019 and Z181100004418004), Beijing Natural Science Foundation (4181004, 4182080, 4184110, 2184131, and Z180011), and Shenzhen Science and Technology Program (Grant No. KQTD20170810105439418), the Natural Science Foundation of Beijing Municipality (4204114), and the Physics Discipline Improvement Program of Zhengzhou University.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

anti-counterfeiting, fluorescent labels, multi-color, stable, ultrathin

Received: February 25, 2021

Revised: June 2, 2021

Published online:

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