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Supplementary Information:

Lead-Free Cs_2PdBr_6 Perovskite-Based Humidity Sensor for Artificial Fruit Waxing Detection

*Wen Ye, Jing-Hui He, Qiang Cao, Xue-Feng Cheng, Chuang Yu, and Jian-Mei Lu**

College of Chemistry Chemical Engineering and Materials Science, Collaborative Innovation Center of Suzhou Nano Science and Technology, National United Engineering Laboratory of Functionalized Environmental Adsorption Materials Soochow University
Suzhou 215123, P. R. China
E-mail: lujm@suda.edu.cn

Experimental Procedures

Synthesis of Cs_2PdBr_6: CsBr (2mmol, TCI, >99% purity) and $PdBr_2$ (1mmol, Aladdin, 99% purity) were dissolved in aqueous HBr (5 mL, Snopharm Chemical Reagent Co., Ltd., ≥40%) solution in three-necked flask oven at 85 °C for 5 min. When precursors were completely dissolved to form a clear solution in HBr, 10 vol% of DMSO (Enox, AR) for HBr was added into the hot precursor solution at 120°C on the hot plate. Immediately, black Cs_2PdBr_6 crystals precipitate was formed by the adding DMSO in the solution and it was cooled down to the room temperature. The crystals were washed with toluene and water for a few times. The crystals were dried in the box oven at 100 °C overnight.[1]

Preparation of oleic acid modified Cs_2PdBr_6 solution: Cs_2PdBr_6 (160 mg) powder was dissolved in 1 mL mixed solvent (DMF/DMSO=1:1) at 50°C to form the precursor solution. 0%, 0.1%, 0.2%, 0.5% and 1% oleic acid in volume was added to propionic acid, respectively. Stir for 30 minutes. Then 200 μL precursor solution was rapidly injected into the propanoic acid (10mL) under vigorous stirring 30 minutes. The obtained black solution was allowed to stand for 120 minutes, and the bottom 1ml solution (precipitate) was taken.

Fabrication of humidity sensor: The Al_2O_3 substrate printed by the Ag-Pd interdigitated electrode (IDES, electrode distance and width is 200 μm) was placed on a heating platform at 100° C. Subsequently, 200 ul Cs_2PdBr_6 solution (precipitation) was added dropwise to the Al_2O_3 substrate. While dripping the solution (precipitation), applied with a brush to form a more uniform film. After the brushing is finished, heating is continued for 5 minutes. The Ag-Pd interdigitated electrodes are fabricated by spraying a metal paste onto a ceramic plate by a metal injection system (MJ-10, Beijing Elite Technology Co. Ltd, China).

Humidity Sensing Characteristics Measurement: The humidity sensing performances were measured through transferring the device into six glass chambers which contained various saturated salt solutions (LiCl, $MgCl_2$, $Mg(NO3)_2$, NaCl, KCl and KNO_3). These six gas-solution equilibrium systems corresponded to relative humidities of 11%, 33%, 54%, 75%, 85% and 95%, respectively.[2] The interdigitated electrodes are wired to a precision impedance analyzer, as depicted in **Fig S5**. The impedance was measured at AC 1 V and the frequency varied from 20 Hz to 1MHz. The sampling time point interval in the impedance-time curve test is 0.383 s. Laboratory temperature to 29°C, humidity 55%.

Fruit waxing and leaves freshness detection: Waxed apples and oranges was purchased from the market. The unwashed fruits was obtained by immersing waxed ones in hot water and washed to remove the surface wax. Subsequently, the washed and unwashed fruits were placed under the constant environmental conditions (29℃, 48 RH%) for 12 h. Similarly, Ginkgo biloba leaves of different freshness on the same tree was collected and placed under the constant environmental conditions (29℃, 48% RH) for 12 hours before test.

Measurements and General Methods: The optical images were captured by a Canon camera. SEM images were characterized using a field emission SEM (FESEM) HITACHI Japan (S-4700) and. TEM experiments were taken on FEI TECNAI G20 instrument. XRD measurements were performed with a multiple crystals X-ray diffractometer (X'Pert PRO, PANalytical). Fourier transform infrared spectroscopy (FTIR) measurements were conducted by using a VERTEX70. TGA experiments were taken on BRUKER TG 209. The impedance of the sensor was measured by the Wayne Kerr 6500B.

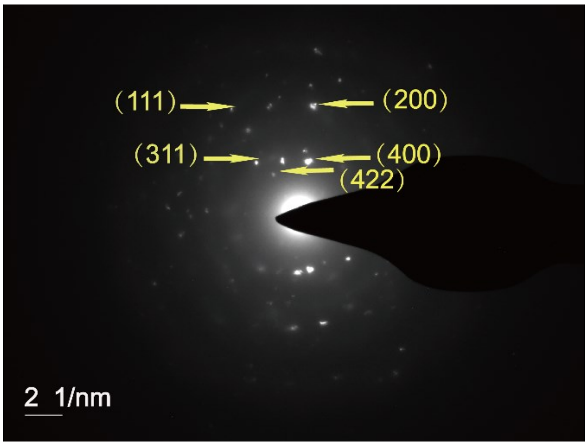

Fig S1. Electron diffraction pattern of the Cs_2PdBr_6 powders.

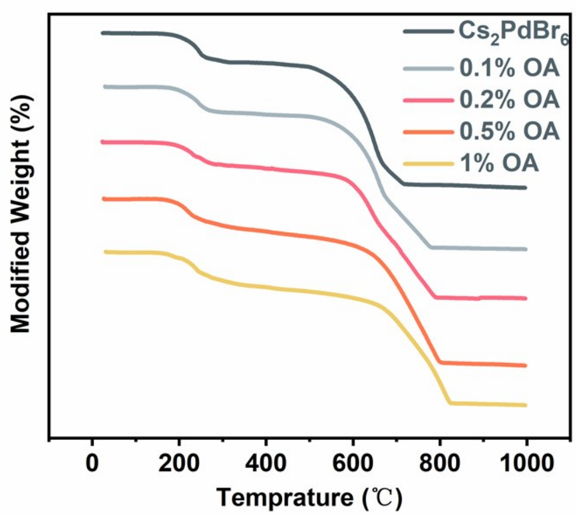

Fig S2. The TGA curves of the Cs_2PdBr_6 modified with different amounts of OA.

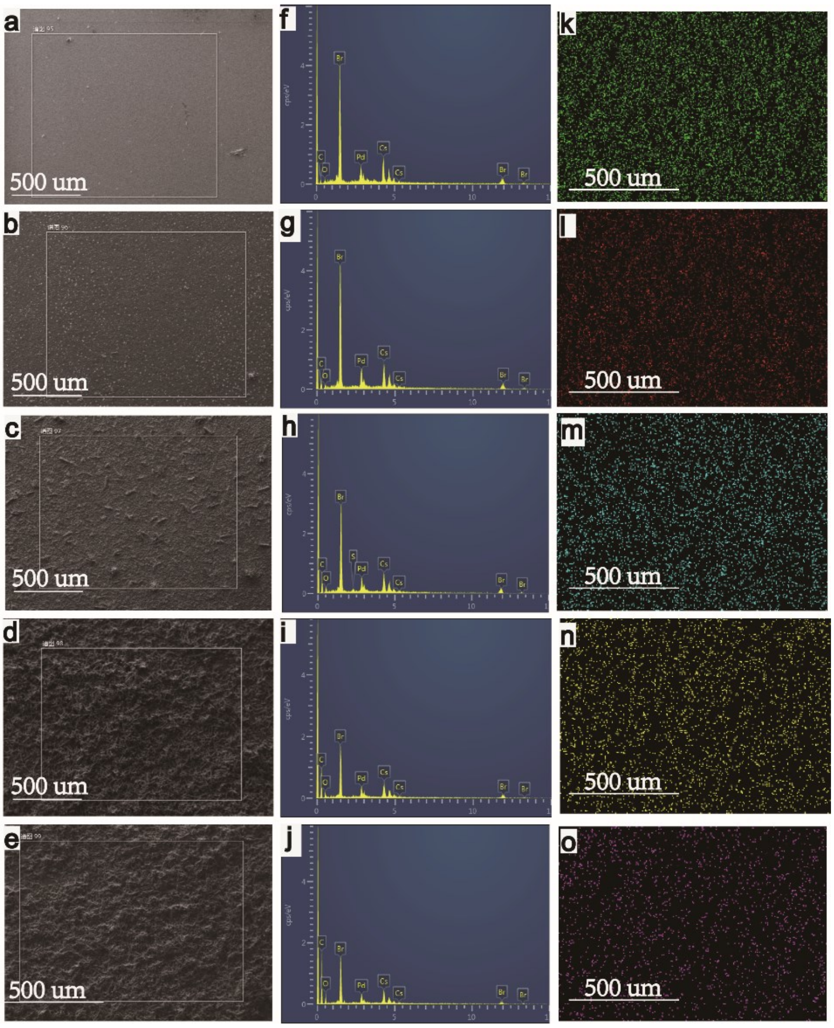

Fig S3. a), b), c), d), and e) are SEM images of Cs_2PdBr_6 brush-coated films with 0% OA modification, 0.1% OA modification, 0.2% OA modification, 0.5% OA modification, and 1% OA modification. f), g), h), i), and j) are EDX analysis images of Cs_2PdBr_6 modified with different amounts of OA. k), l), m), n), and o) are distribution of Cs_2PdBr_6 film C, Br, Cs, Pd and O element content after 0.2% OA oleic acid modification.

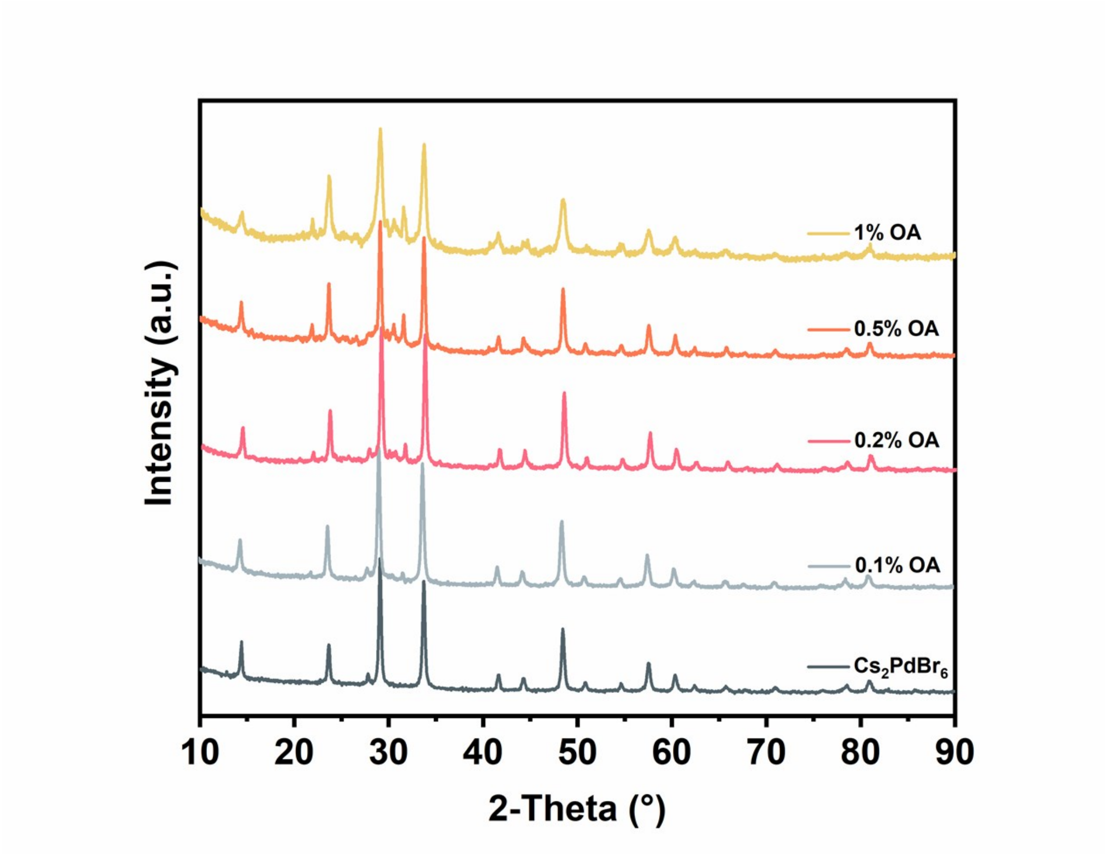

Fig S4. The XRD curves of the Cs_2PdBr_6 modified with different amounts of OA.

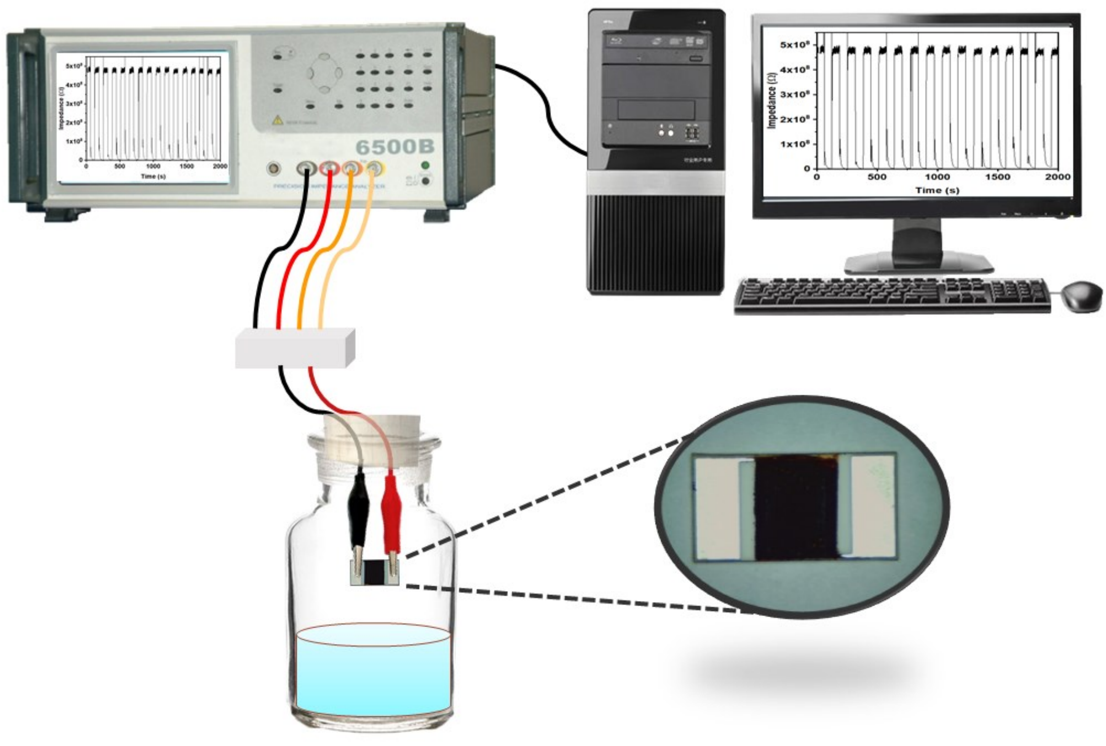

Fig S5. Schematic diagram of real-time humidity sensing setup.

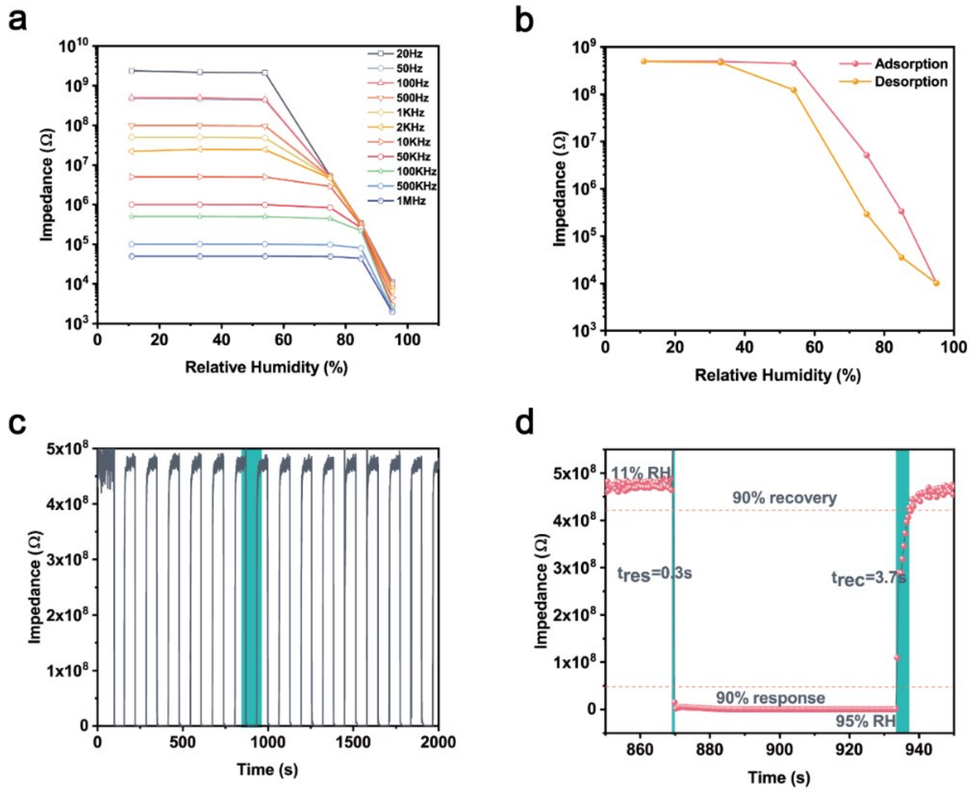

Fig S6. a) Typical humidity sensing performances of Cs_2PdBr_6-0.1% OA: a) Impedance versus RH curves with frequency from 20 Hz to 1 MHz. b) The humidity hysteresis at 100 Hz. c) The dynamic response from 11% to 95% RH. d) Response and recovery time in c).

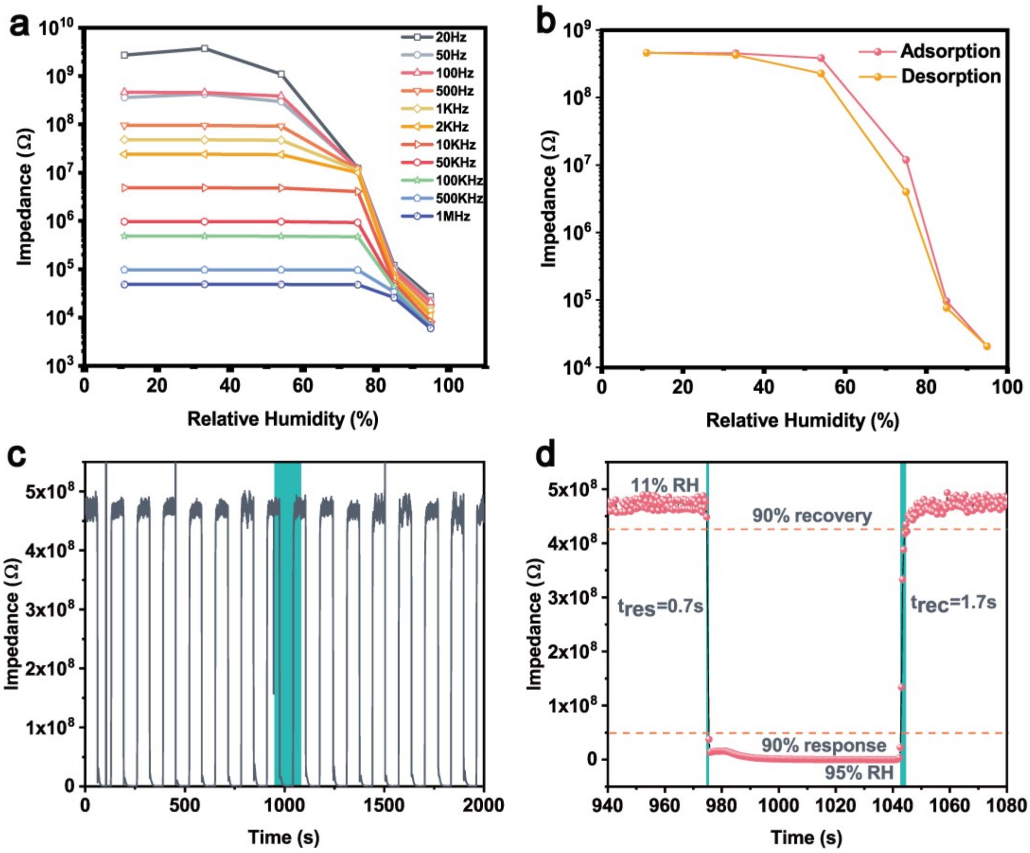

Fig S7. a) Typical humidity sensing performances of Cs_2PdBr_6-0.2% OA: a) Impedance versus RH curves with frequency from 20 Hz to 1 MHz. b) The humidity hysteresis at 100 Hz. c) The dynamic response from 11% to 95% RH. d) Response and recovery time in c).

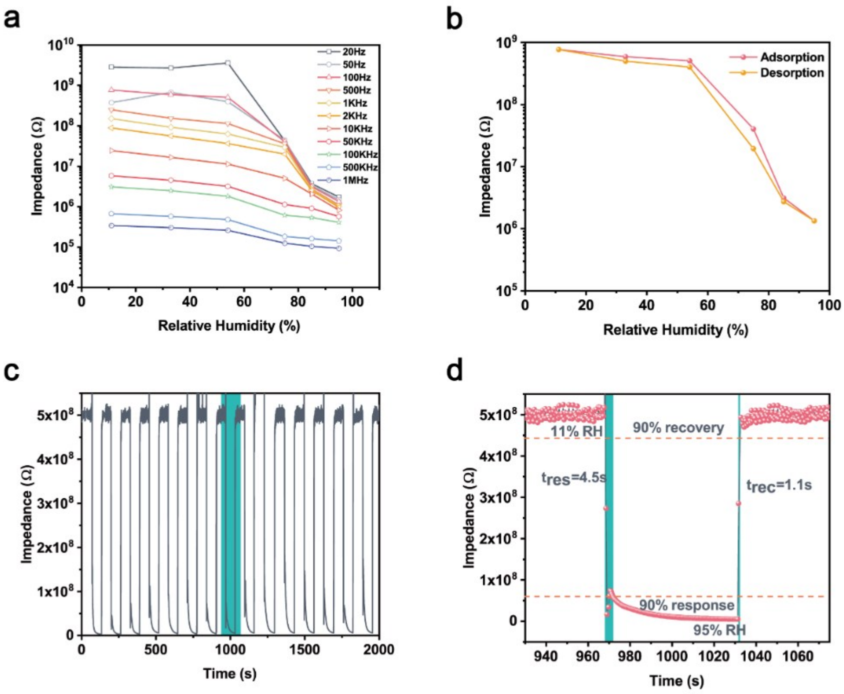

Fig S8. Typical humidity sensing performances of Cs_2PdBr_6-0.5% OA: a) Impedance versus RH curves with frequency from 20 Hz to 1 MHz. b) The humidity hysteresis at 100 Hz. c) The dynamic response from 11% to 95% RH. d) Response and recovery time in c).

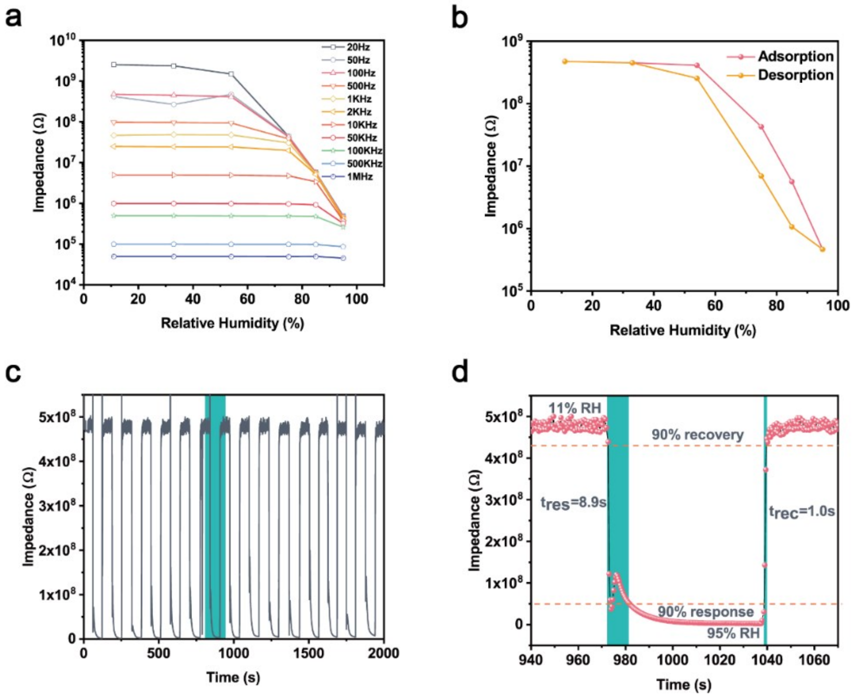

Fig S9. Typical humidity sensing performances of Cs_2PdBr_6-1% OA: a) Impedance versus RH curves with frequency from 20 Hz to 1 MHz. b) The humidity hysteresis at 100 Hz. c) The dynamic response from 11% to 95% RH. d) Response and recovery time in c).

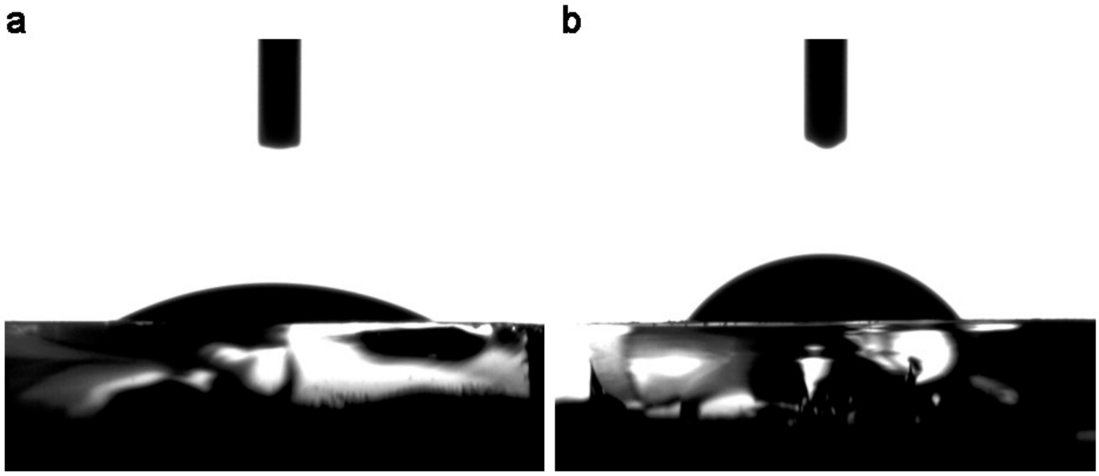

Fig S10. The contact angle tests of brush-coated films a) without OA and b) with OA modified Cs_2PdBr_6.

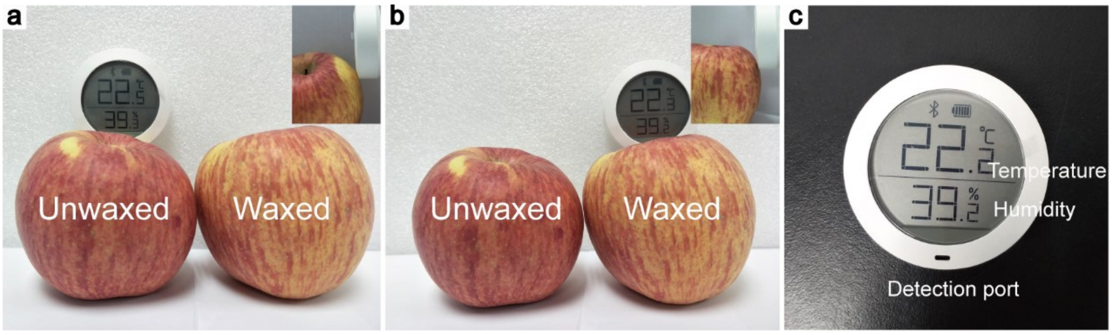

Fig S11. Photographs of commercial detectors detect waxed and unwaxed fruits.

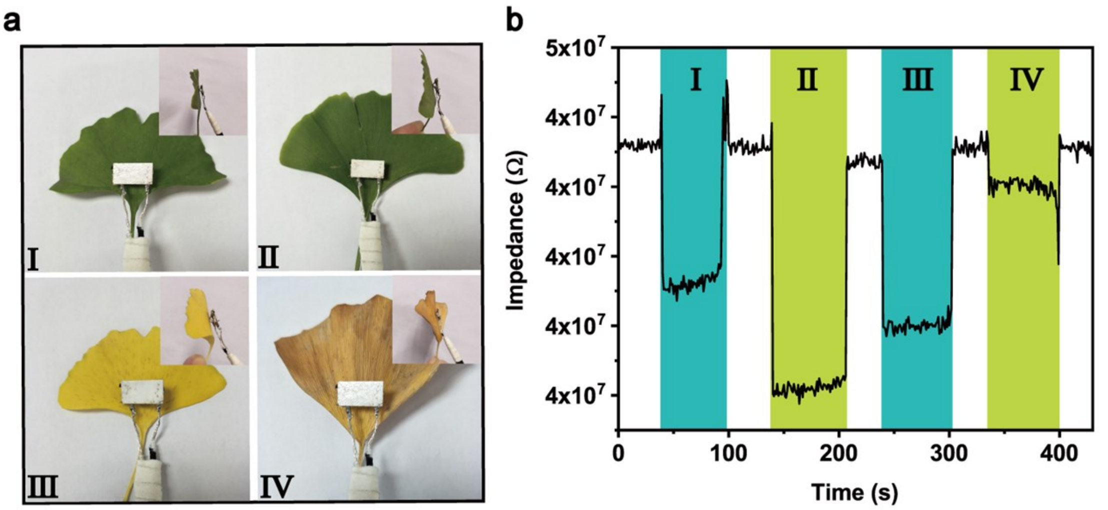

Fig S12. a) Optical image of ginkgo leaves with different degrees of freshness, figs I, II, III and IV represent leaves from newborn to withered. b) Dynamic responses of the 0.2% OA modified Cs_2PdBr_6 humidity sensor to leaves with different degrees of freshness at 29°C and 48 RH%.

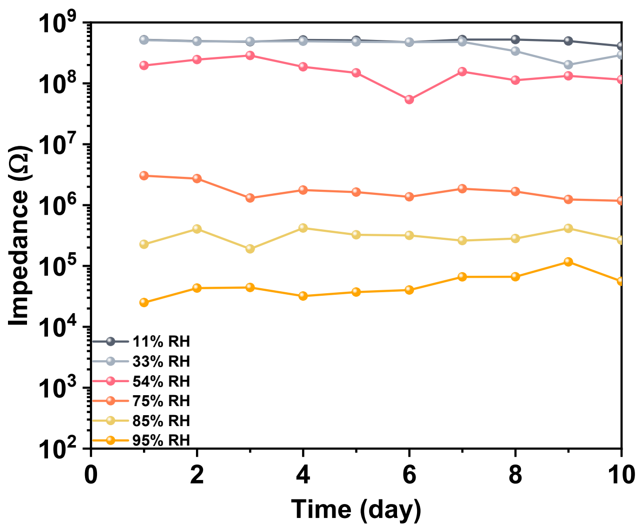

Fig S13. The long-term stability of the sensor (aged under the exposure of the ambient (29 °C, 55% RH)) toward different RH values.

Table S1. Comparison of the performance of different perovskite modification humidity sensors.

Sensing Materials	Impedance Variation (W)	Response/recovery Time (s)	Maximum Hysteresis	Work Range (% RH)
Cs_2PdBr_6-0%OA	10^3-10^9	0.4/6.0	14.10%	11-95
Cs_2PdBr_6-0.1%OA	10^4-10^9	0.3/3.7	10.50%	11-95
Cs_2PdBr_6-0.2%OA	10^4-10^9	0.7/1.7	2.20%	11-95
Cs_2PdBr_6-0.5%OA	10^6-10^9	4.5/1.1	3.10%	11-95
Cs_2PdBr_6-1%OA	10^6-10^9	8.9/1.0	8.60%	11-95

References

1. N. Sakai, A. A. Haghighirad, M. R. Filip, P. K. Nayak, S. Nayak, A. Ramadan, Z. Wang, F. Giustino and H. J. Snaith, *J Am Chem Soc*, 2017, **139**, 6030-6033.
2. L. Greenspan, *Journal of Research of the National Bureau of Standards Section a-Physics and Chemistry*, 1977, **81**, 89-96.