Supporting Information

Enhancing Bromine-Doped $CuBiI_4$ Photodetectors through Charge Dynamics and Conductivity Analysis

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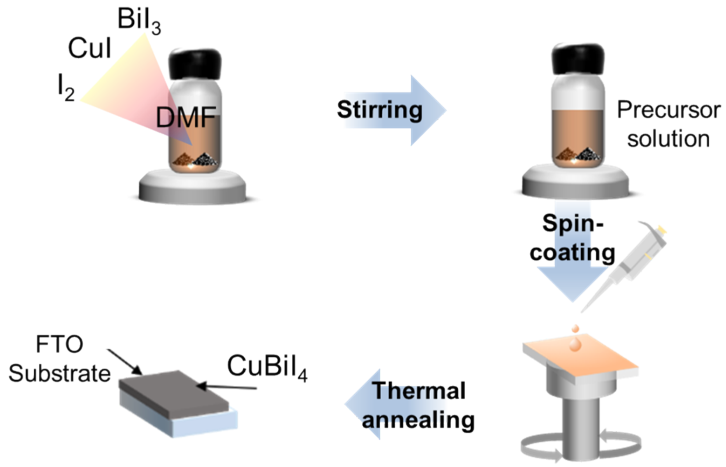

Figure S1. Spin-coating process to $CuBiI_4$ films: CuI, BiI_3 and I_2 were dissolved in DMF solution under stirring for 2-4 hours, which resulted in a precursor solution for the spin-coating process. After the thermal annealing, the grey-black films were obtained.

For Br-doped $CuBiI_4$ films, a portion of CuI was replaced by CuBr from the beginning, keeping all other conditions the same.

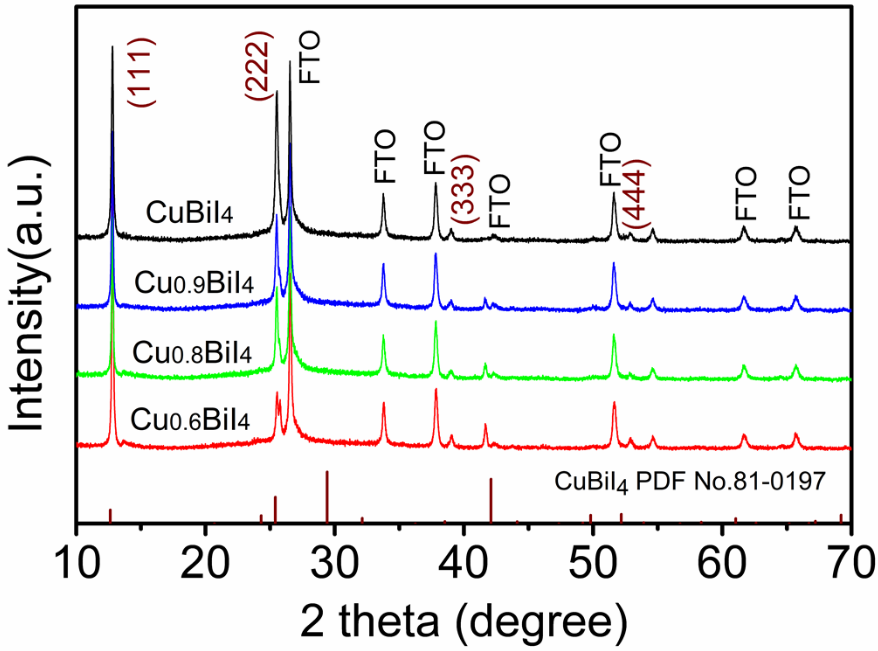

Figure S2. The XRD patterns of $CuBiI_4$ with various Cu/Bi ratios of 1:1, 0.9:1, 0.8:1 and 0.6:1. Pure $CuBiI_4$ crystalline films could be prepared, which had a cubic structure (JCPDS card. No. 81-0197).

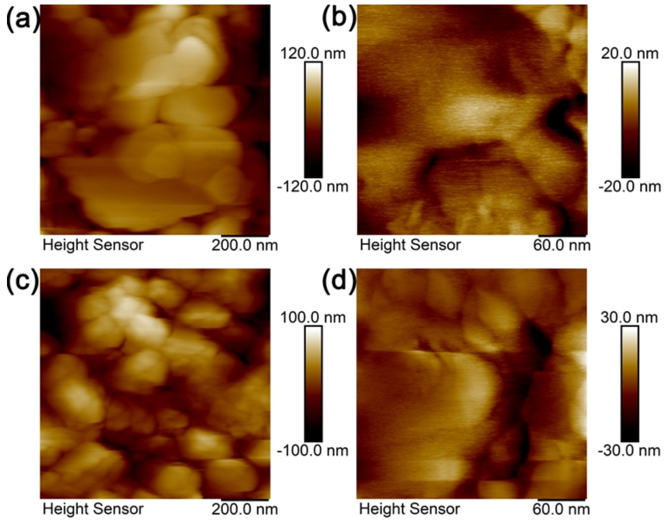

Figure S3. AFM images of the undoped (a & c) and Br0.2 (b & d) doped $CuBiI_4$ films.

Table S1. The optoelectronic parameters of the $CuBiI_4$ photodetector.

$CuBiI_4$	Responsivity (A/W)	Response time τ_{rise} (s)	Response time τ_{fall} (s)	On/off ratio
Undoped	8.52×10^{-5}	0.24	0.20	31.2
Br0.1	2.01×10^{-4}	0.23	0.17	41.3
Br0.2	3.41×10^{-4}	0.2	0.15	40.6
Br0.3	1.70×10^{-4}	0.24	0.17	20.4
Br0.4	1.39×10^{-5}	0.12	0.15	65

Note: measured under a bias of 3 V and white LED illumination (100 mW/cm^2).

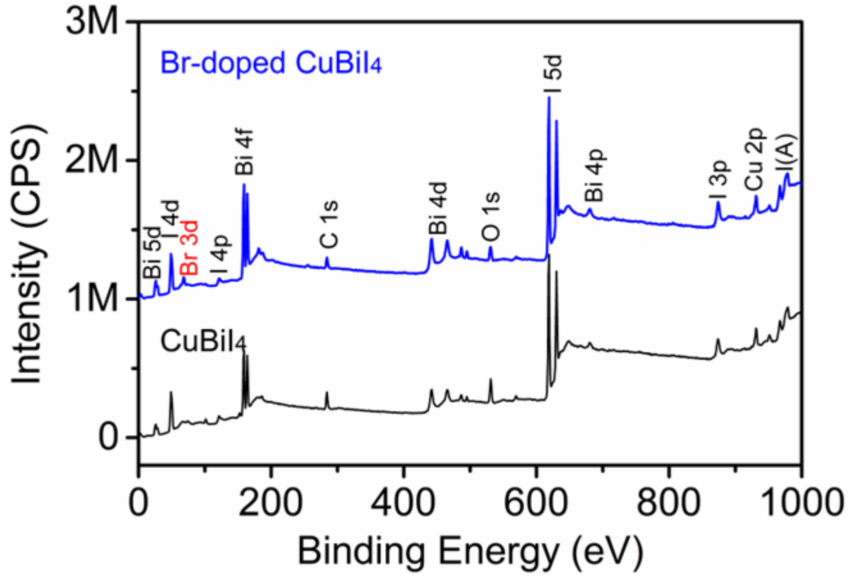

Figure S4. The X-ray photoelectron spectroscopy (XPS) survey spectra confirmed the presence of essential elements, including copper (Cu), bromine (Br), and iodine (I), in the sample. The doped $CuBiI_4$ films showed a conspicuous peak ~69 eV, which was ascribed to Br3d.

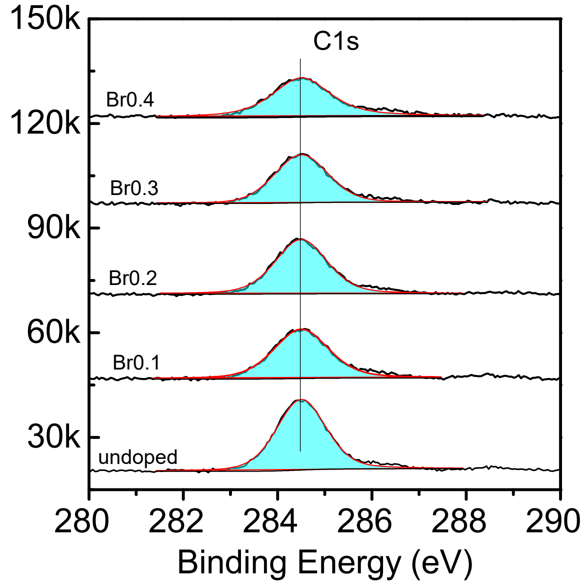

Figure S5. The XPS spectra of C1s on undoped, Br-doped $CuBiI_4$ films.

$CuBiI_4$ Films	Br3d	Cu2p 3/2	Bi4f 7/2	I3d5/2	Cu/Bi/I/Br Ratio
S.F.	0.59	4.3	2.8	4.4	-
undoped	-	3.00×10^{4}	1.09×10^{5}	2.84×10^{5}	0/0.433/2.415/4.00
Br0.1	7.55×10^{3}	2.96×10^{4}	1.44×10^{5}	3.42×10^{5}	0.304/2.271/3.435/0.565
Br0.2	8.39×10^{3}	2.75×10^{4}	1.26×10^{5}	2.83×10^{5}	0.327/2.291/3.274/0.726
Br0.3	1.22×10^{3}	1.95×10^{4}	1.39×10^{5}	2.77×10^{5}	0.216/2.374/3.008/0.992
Br0.4	1.47×10^{3}	3.05×10^{4}	1.57×10^{5}	3.06×10^{5}	0.300/2.366/2.945/1.055

Table S2. The element ratio on the undoped and Br-doped $CuBiI_4$ surfaces.

S.F.: sensitive factor data is used from reference[1].

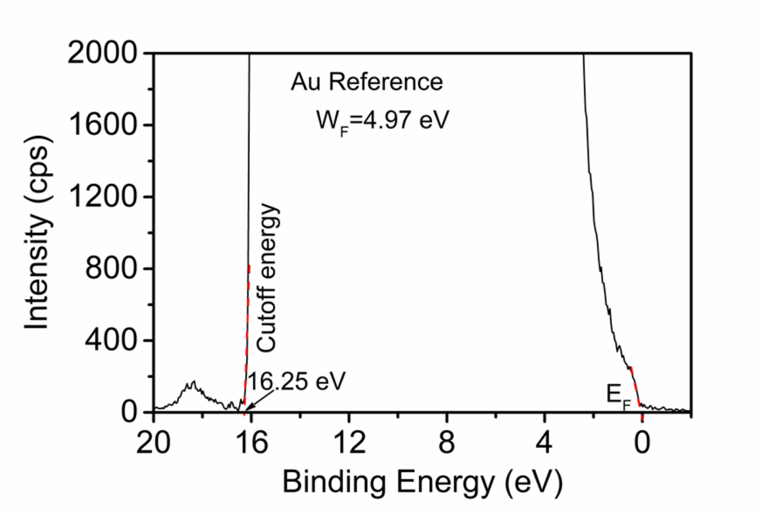

Figure S6. UPS of Au standard film. The work function of Au was 4.97 eV, which was slightly lower than the 5.31 eV on Au (111)[2].

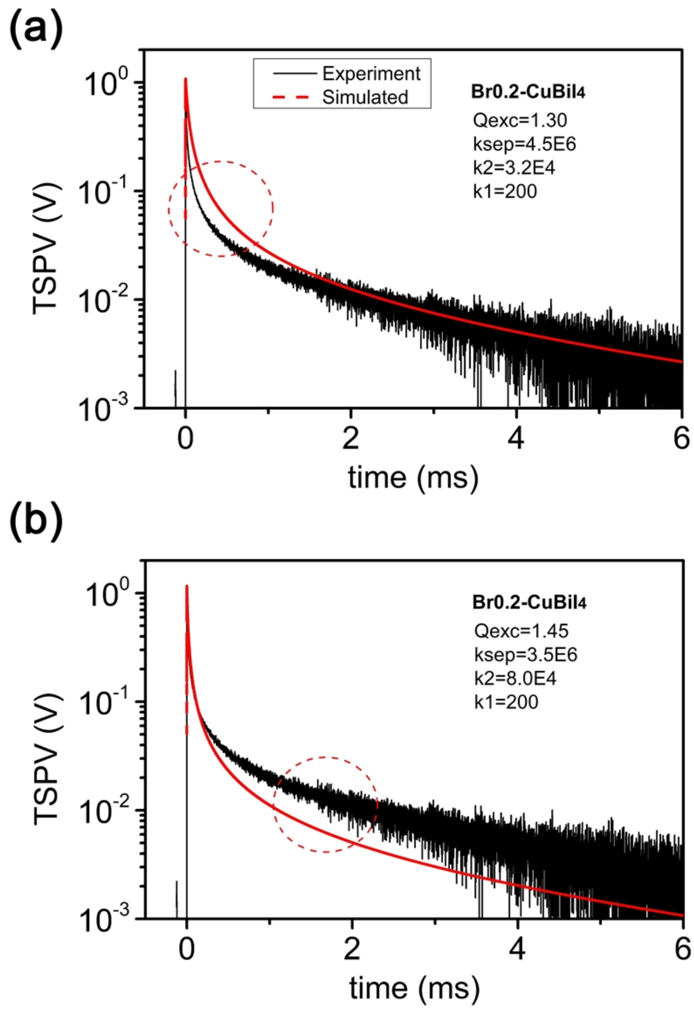

Figure S7. The simulation curves are based on 1st-order and 2nd-order recombination with different parameters: (a) smaller k_2 rate constant (3.2×10^4) shows large discrepancy in the early stage due to the slower consumption of surface charge; (b) larger k_2 rate constant (8.0×10^4) shows large discrepancy in the late stage due to the faster consumption of surface charge.

Table S3. The rate constants calculated based on the Eq. (6) in the paper and the TSPV curves.

$CuBiI_4$ Films	k_{sep} (1^{st})	K_3 (3^{rd})	k_1 (1^{st})	t_{max}	Q_{exc}
undoped	3.1×10^{6}	2.9×10^{5}	460	8.2×10^{-7}	1.36
Br0.1	3.1×10^{6}	7.5×10^{5}	480	6.4×10^{-7}	1.47
Br0.2	2.6×10^{6}	6.5×10^{5}	500	6.6×10^{-7}	1.8
Br0.3	3.6×10^{6}	$2.\times10^{5}$	900	7.5×10^{-7}	1.05
Br0.4	2.7×10^{6}	3.2×10^{6}	700	6.9×10^{-7}	0.70

Note:

$$\frac{dQ_{sep}}{dt} = k_{sep}Q_{exc} - k_n Q_{sep}^n - k_1 Q_{sep} \quad (6)$$

The Q_{exc}, Q_{sep}, k_{sep}, k_n and k_1 are the initial photogenerated charges in bulk shortly after the transient laser excitation, the surface charge transported from bulk through separation, the apparent rate constant of charge separation (1^{st}-order), the rate constant of multiple-charge (n^{th}-order) decay reaction and the rate constant of an apparent single charge (1^{st}-order) decay reaction, respectively.

References:

1. C. D. Wagner, C. D. Wagner and G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Data for Use in X-ray Photoelectron Spectroscopy*, Perkin-Elmer, 1979.
2. W. M. Haynes, *CRC Handbook of Chemistry and Physics*, CRC Press, 2014.