Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting information for

Heterointerface engineering of layered double hydroxide/$MAPbBr_3$ heterostructures enabling tunable synapse behaviors in a two-terminal optoelectronic device

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1. Methods

1.1 Materials

Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), hexamethylenetetramine (HMT), lead bromide ($PbBr_2$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), and oleylamine (OLA) were purchased from Sigma-Aldrich, USA. Methylammonium bromide (MABr) was purchased from Xi'an Polymer Light Technology Co., Ltd., China. Oleic acid (OA) was purchased from TCI, Japan. Toluene and N, N-dimethyl formamide (DMF) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China. All reagents were used as received without any purifications.

1.2 Preparation of MgAl-LDH nanoplates

MgAl-LDH nanoplates were prepared by the hydrothermal method followed by anion exchange. A mixture of $Al(NO_3)_3{\cdot}9H_2O$ (0.01 mol), HMT (0.026 mol), $Mg(NO_3)_2{\cdot}6H_2O$ (0.02 mol) and water (80 mL) was heated in an autoclave at 140 °C for 12 h. The product was washed and vacuum-dried at 60℃. Then, 100 mg of the product, $NaNO_3$ (0.25 mol) and HNO_3 (5 mmol) were dissolved in 100 mL water, and mixed thoroughly by shaking under N_2 atmosphere for 24 h. The obtained MgAl-LDH nanoplates were washed by water and dried for further use.

1.3 Preparation of $MAPbBr_3$ nanocrystals

$MAPbBr_3$ nanocrystals were prepared by a ligand-assisted reprecipitation method. Typically, $PbBr_2$ (0.2 mmol), MABr (0.2 mmol), OLA (18.2 µL) and OA (0.5 mL) were added into 5 mL DMF and mixed for 15 min. 100 µL of the mixed solution was added dropwise into 5 mL toluene under shaking. The green product was washed with toluene for three times and then redispersed in 1 mL toluene.

1.4 Preparation of LDH-$MAPbBr_3$ heterostructures

A mixture of the $MAPbBr_3$ stock solution (0.2 mL), LDH (2.5 mg) and toluene (5 mL) was vigorously stirred for 10 min to realize the formation of LDH-$MAPbBr_3$ heterostructures.

1.5 Device fabrication

LDH-$MAPbBr_3$ heterostructures and other control samples were dropped-casted on Au interdigitated electrodes (Mecart Sensor Tech, China) deposited on SiO_2 (300 nm)/Si substrate. Both the width and the gaps between electrode branches were 10 µm.

1.6 Characterizations

The crystal structure and morphology of the various samples were characterized by X-ray diffraction (XRD, with Cu Kα radiation at λ = 1.54 Å, SmartLab Rigaku, Japan), scanning electron microscopy (SEM, JEOL JSM-7800F, Japan), transmission electron microscopy (TEM, JEOL 2100 Plus, Japan), and high-resolution transmission electron microscopy (HRTEM, JEOL 2100F, Japan), respectively. The optical properties of samples were characterized by ultraviolet-visible spectrophotometer (Shimadzu UV-1750, Japan), fluorescence spectrometer (Hitachi F4600, Japan), ultraviolet photoelectron spectrometer (Thermo ESCALAB 250XI, USA), and fluorescence spectrophotometer (FLS-980, Edinburgh Instruments). The optoelectrical tests were completed by the semiconductor characterization system (Keithley 4200SCS, USA) coupled with a laser source (Thorlabs DC2200, USA) under different humidity. The light intensity and relativity humidity were adjusted by using a laser power meter (Sanwa LP10, Japan) and a hygrometer (Anymetre TH21E, China), respectively. The surface potential was tested by a KPFM (Bruker Dimension ICON with Nanoscope V, Germany). The impedance measurement was completed by an electrochemical station (Autolab 86567, USA).

1.7 Neuromorphic computing simulation

A multilayer perceptron (MLP) simulator NeruroSimV3.0 was used to recognize the MNIST handwritten digital images. The tailored MNIST graphs (20 × 20 pixels) were entered into the 400 input neurons with output of 10 classes of digits from 10 output neurons. After the 2-layer MLP neural network was constructed, the nonlinear weight update behavior in the simulation was emulated by the following equations[1]:

$$G_{LTP} = B\left(1 - e^{\left(-\frac{P}{A}\right)}\right) + G_{min} \tag{1}$$

$$G_{LTD} = -B\left(1 - e^{\left(\frac{P - P_{max}}{A}\right)}\right) + G_{max} \tag{2}$$

$$B = (G_{max} - G_{min})/\left(1 - e^{\left(-\frac{P_{max}}{A}\right)}\right) \tag{3}$$

where G_{LTP} and G_{LTD} are the conductance for long-term potentiation and long-term depression, respectively, and G_{max}, G_{min} are the maximum conductance, minimum conductance. *P* and P_{max} are the number of spikes and the maximum of *P*. *A* is the parameter related to the nonlinearity (NL), and *B* is a fitting constant. To simplify the simulation, the NL for the long-term depression is the negative of that of the long-term potentiation. The NL was extracted from the experimental data by trying the value of *B* to find the best fit of weight update, then looking up the table in

NeruroSimV3.0 to obtain the NL. Subsequently, stochastic gradient decent method is used to update the weight in back propagation in this simulation.

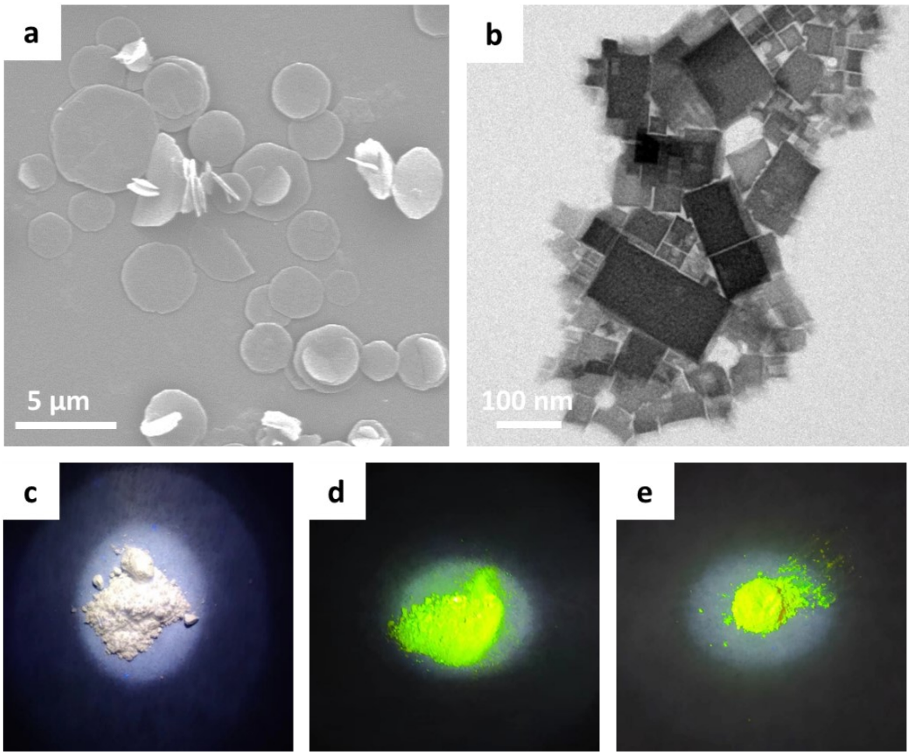

Figure S1. a) SEM image of MgAl-LDH. b) TEM image of $MAPbBr_3$. Optical images of c) MgAl-LDH, d) $MAPbBr_3$ and e) LDH-$MAPbBr_3$ exposed under 405 nm laser.

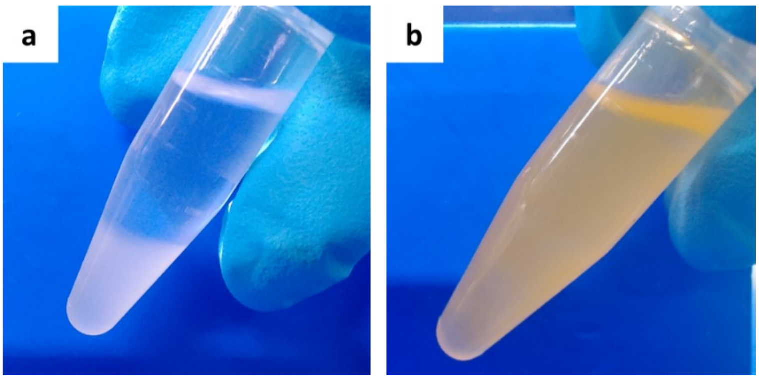

Figure S2. Dispersions of a) LDH and b) LDH-$MAPbBr_3$ in toluene.

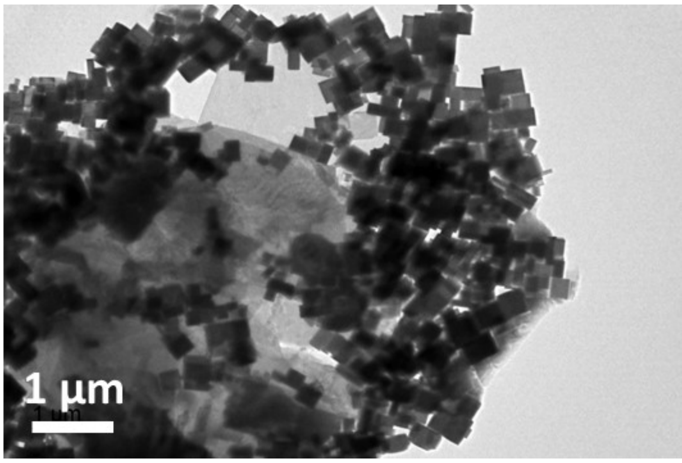

Figure S3. TEM image of LDH-$MAPbBr_3$ in which the surface ligands oleylamine/oleic acid on $MAPbBr_3$ were not largely removed by washing.

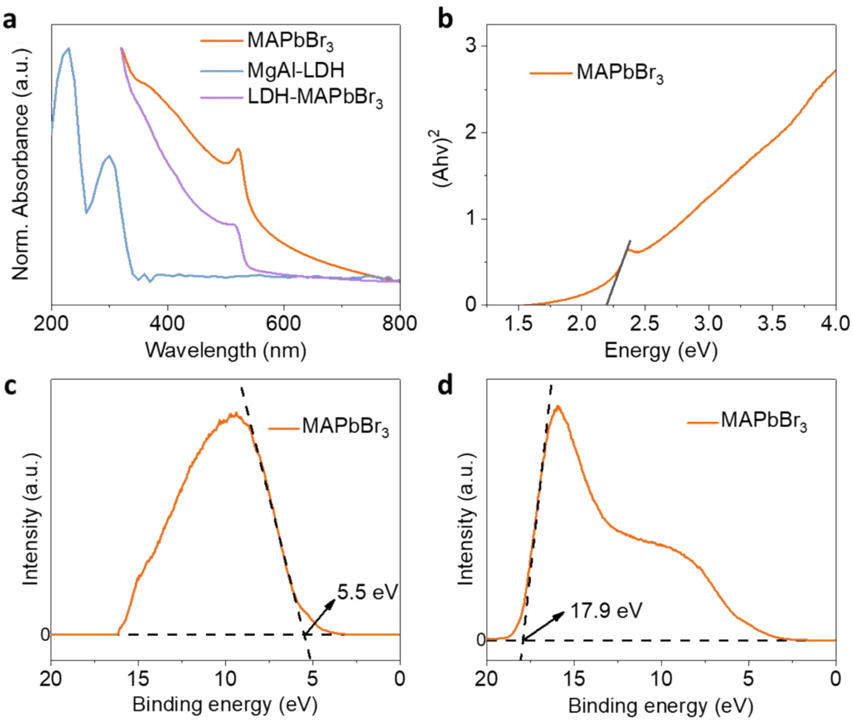

Figure S4. a) UV-vis adsorption spectra of LDH, $MAPbBr_3$ and LDH-$MAPbBr_3$. b) Tuac plot of $MAPbBr_3$. UPS spectra of $MAPbBr_3$ measured c) under 0 eV bias to acquire its valance band maximum (VBM) position and d) under -5 eV bias to acquire its work function.

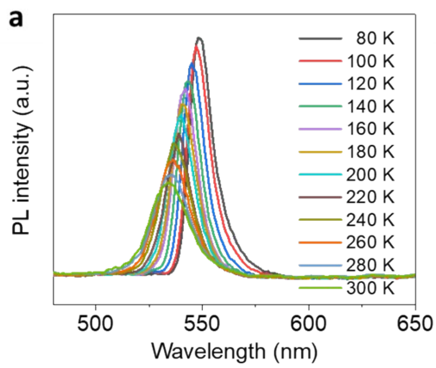

Figure S5. PL spectra of a) $MAPbBr_3$ and b) LDH-$MAPbBr_3$ at varied temperatures.

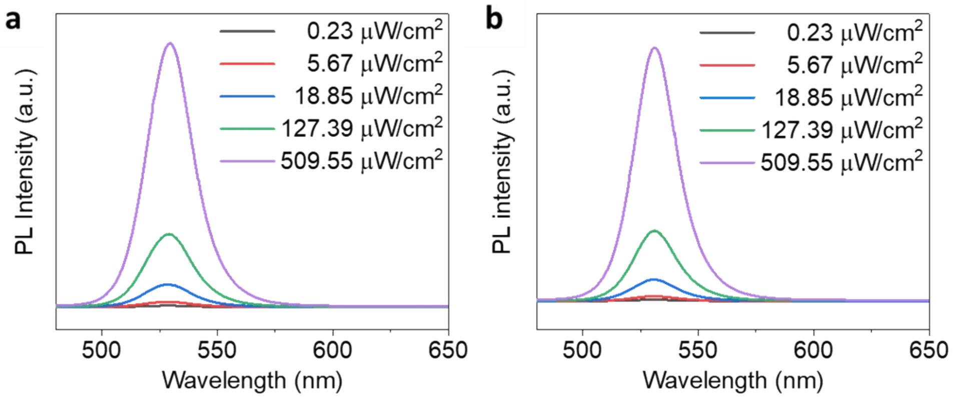

Figure S6. PL spectra of a) $MAPbBr_3$ and b) LDH-$MAPbBr_3$ under varied power intensities.

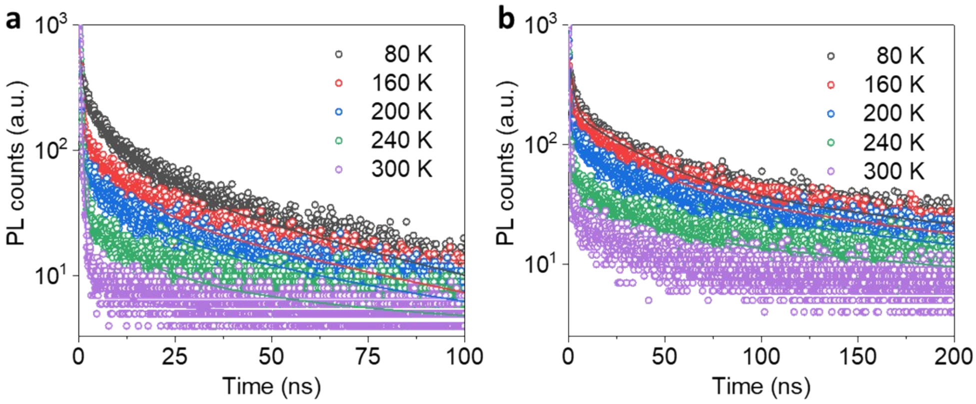

Figure S7. PL lifetime of a) $MAPbBr_3$ and b) LDH-$MAPbBr_3$ at varied temperatures.

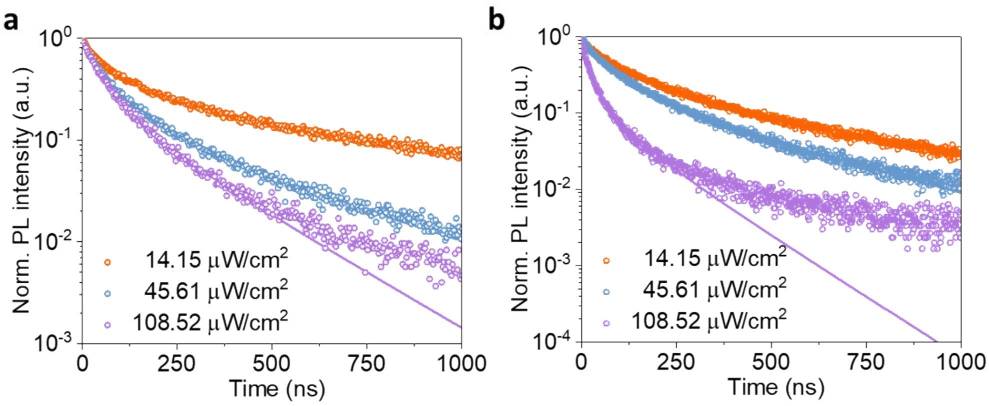

Figure S8. PL decay and their fitting curves of a) $MAPbBr_3$ and b) LDH-$MAPbBr_3$ under varied power intensities.

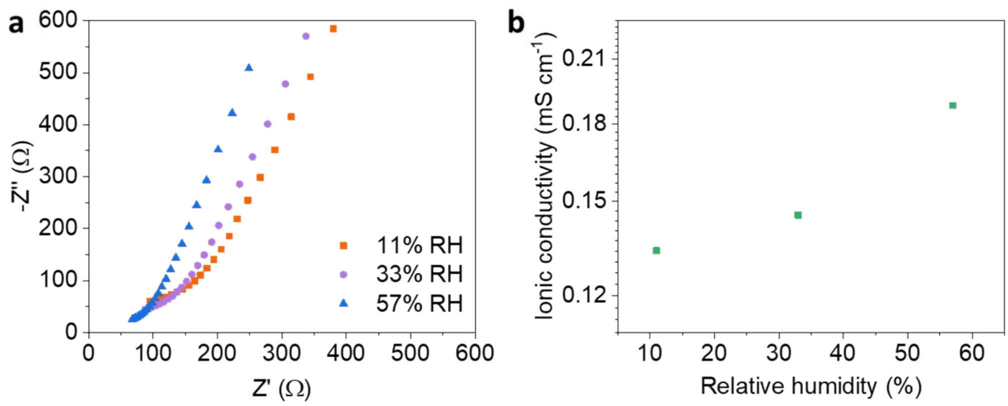

Figure S9. Humidity-dependent a) impedance plots of LDH and b) the corresponding ionic conductivity. (LDH powders were pressed into a pellet and then measured by an electrochemical station. Ionic conductivity was calculated using the equation: $\sigma = L/(R*S)$, where L and S are the thickness and cross-sectional area of the pellet, respectively, and R was extracted directly from the impedance plots.[2])

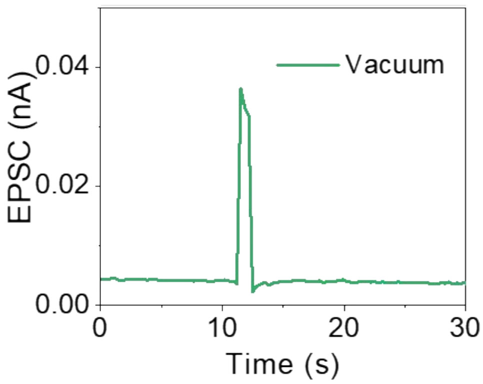

Figure S10. Photo response of LDH-$MAPbBr_3$ under vacuum condition.

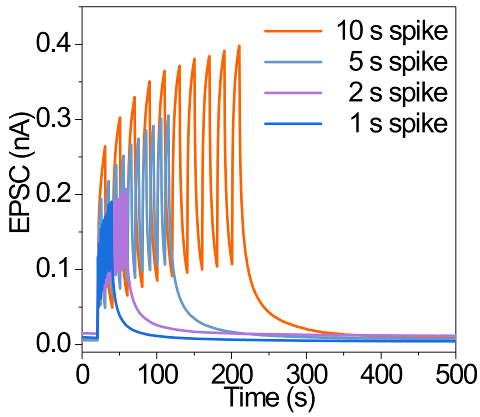

Figure S11. Optical duration modulated synaptic plasticity of LDH-$MAPbBr_3$ optoelectronic synapse.

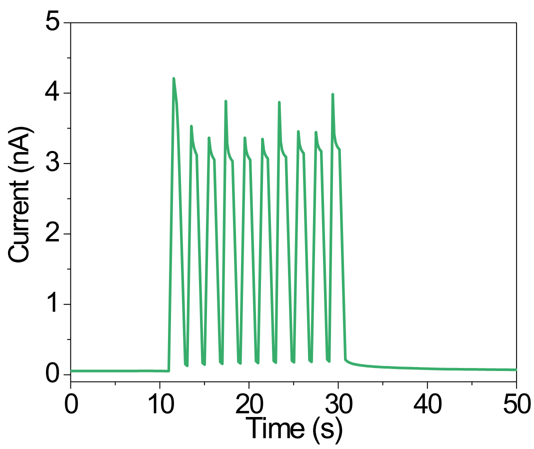

Figure S12. Photoresponse of a device based on randomly assembled LDH-$MAPbBr_3$ composite.

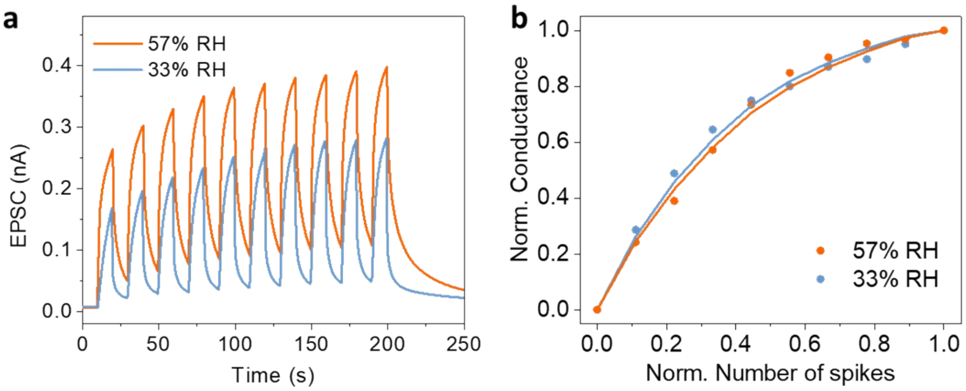

Figure S13. a) EPSC responses of LDH-$MAPbBr_3$ synapse exposed to ten successive light pulses and b) their fitting curves of LTP behavior with nonlinearity (NL) of 2.9, 2.6 for 33% RH and 57% RH, respectively.

Table S1 Parameters of the fitted PPF index under various humidity conditions.

Humidity conditions	C_0	C_1	C_2	τ_1 (s)	τ_2 (s)
57% RH	91.5	61.8	31.5	1.9	**114.8**
33% RH	100.5	77.4	9.1	1.1	**15.2**
11% RH	100.6	21.4	7.0	2.0	**8.4**

Table S2 Comparison of performance of solution-processed two-terminal optoelectronic synapse devices upon light stimuli.

Materials	Humidity	PPF	STP/STM	LTP/LTM	Ref.
$CsPbBr_3$	/	133%*	Y	Y	3
$MAPbI_3$:Si NCs	/	137%	Y	/	4
P3HT	/	131.6%	Y	Y	5
ZnO/P3HT	/	149%	Y	Y	6
$FA_{0.9}Cs_{0.1}PbI_{3-x}Cl_x$ /spiro-MeOTAD	/	125%*	Y	Y	7
$SnO_2/MAPbI_3$	/	155%*	Y	/	8
DPPDTT	/	121%	Y	Y	9
$(PEA)_2SnI_4$	/	153%*	Y	/	10
N:ZnO/MoS_2	/	132%*	/	Y	11
Au/LSNO/Au	/	138%*	Y	Y	12
SnO_2	Humid air	125%*	/	/	13

$Cs_2AgBiBr_6$/ P(VDFTrFE)/ pentacene	60% RH	123%	/	Y	[14]
LDH-$MAPbBr_3$	57% RH	158%	Y	Y	This work

* Data estimated from the references

short-term memory (STM), long-term memory (LTM)

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