Gas Induced Conversion of Hybrid Perovskite Single Crystal to Single crystal for Great Enhancement of Their Photoelectric

Properties

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Photoelectric properties

Detailed Description of Experimental Procedures

Materials growth

All the analytical-grade reactants of PbO, Dimethylamine hydrochloride ($C_2H_7N.HCl$), butylamine, hexylamine, octylamine, Guanidine Hydrochloride, H₃PO₂ solution and HI solution were purchased from Sinopharm Co. Ltd. and used without further purification. DAPbI₃ single crystals were prepared using a temperature lowering method. Briefly, 0.81 g of C₂H₇N.HCl and 2.07 g PbO were mixed and dissolved in HI solution. Then the mixture was heated to 90 °C using oil bathing until the reactants dissolved completely. Then the temperature was lowered to the room temperature, and got the DAPbI₃ single crystals. Other single crystals were grown by same method. The single crystals were collected for subsequent experiments. Methylamine (CH₃NH₂) gas was generated using a commercially purchased CH₃NH₂ (99%) water solution (25-30 wt%). DAPbI₃ thin films were prepared by spin coating a 30wt% DAPbI₃ solution in DMF solution at 2000 rpm for 40 s, followed by thermal annealing at 100 °C for 10 min. The MA_{0.2}DA_{0.8}PbI₃ single crystals and its thin films were fabricated by placing the DAPbI₃ single crystals and their thin films in CH₃NH₂ gas atmosphere for several hours at 120 °C, respectively.

Materials Characterization

Powder X-ray diffraction and Single-crystal X-ray diffraction studies. Singlecrystal X-ray diffraction and powder X-ray diffraction measurements were depicted elsewhere ^[1,2], as follows. X-ray powder diffraction (XRD) patterns of polycrystalline powder were carried out on a Bruker-AXS D8 Advance X-ray diffractometer with CuKal radiation ($\lambda = 1.54186$ Å) in the range of 10-90° (20) with a step size of 0.004°. Single crystals structures were determined by Bruker SMART APEX-II diffractometer equipped with a CCD detector (graphite-monochromatized Mo-Ka radiation, $\lambda = 0.71073$ Å) at 296 K. Data integration and cell refinement were performed using the APEX2 software^[3]. The structure was analyzed by direct methods and refined using the SHELXTL 97 software package ^[4]. All nonhydrogen atoms of the structure were refined with anisotropic thermal parameters, and the refinements converged for Fo2> 2σ IJFo2). All the calculations were performed using SHELXTL crystallographic software package ^[4]. Symmetry analysis on the model using PLATON^[5] revealed that no obvious space group change was needed. In the refinement, the commands EDAP and EXYZ were used to restrain some of the related bond lengths and bond angles.

Elements analysis measurement. Elements analysis of $MA_{0.2}DA_{0.8}PbI_3$ and $(MA_{0.32}BA_{0.68})_2PbI_4$ by combustion method was carried out using an elemental analyzer (Vario el Z III Z III).

UV-vis-NIR diffuse reflectance spectra measurements. UV–vis-NIR diffuse reflectance spectroscopy was carried out using a conventional UV/Vis spectrometer (Hitachi U-4100) equipped with an integrating sphere over the spectral range 200-1200 nm. The DAPbI₃, MA_{0.2}DA_{0.8}PbI₃, BA₂PbI₄ and (MA_{0.32}BA_{0.68})₂PbI₄ single crystals were dried and grinded into powders. A BaSO4 plate was used as the standard (100% reflectance). The absorption spectrum was calculated from the reflectance spectrum using the Kubelka-Munk function: α /S= (1–R)²/(2R),^[6] where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.

Photoluminescence (PL) measurements, the 450 nm excitation light from a monochromator with Xenon lamp (50 W) as light source was focused on the sample

through an optical chopper (SRS 540). The PL signal was collected with a photomultiplier (PMTH-S1-CR131) and DSP lock-in amplifier (SRS 830).

Time-resolved photoluminescence spectra measurements. Time-resolved photoluminescence spectra measurements were performed on a FLS920 Combined Fluorescence Lifetime and Steady State Spectrometer (Edinburgh, U.K.) which is synchronous equipped with EPL picosecond pulsed laser (445±10 nm).

Thermogravimetric analysis Measurements. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a TGA/DSC1/1600HT analyzer (METTLER TOLEDO Instruments). The DAPbI₃ and MA_{0.2}DA_{0.8}PbI₃ samples were placed in a platinum crucible, and heated at a rate of 10 °C min⁻¹ from room temperature to 800 °C under flowing nitrogen gas.

SCLC and Hall Effect measurements: All current–voltage measurements were carried out by Keithley 4200 semiconductor parameter analyser. The $MA_{0.2}DA_{0.8}PbI_3$ single crystals with the thickness of about 0.17 mm were also used for the measurements of Hall Effect. All of them were deposited with silver conduction paste as the electrodes. The mobility measurement was performed at room temperature on a 4-probe sample holder placed between the plates of an electromagnet on Ecopia HMS-5000 instrument. The magnetic field intensity was at 0.5 T.

Photoresponse measurement. A pair of interdigitated Au-wire electrodes was integrated to collect the current, with each electrode consisting of a group of 8 fine Au wires (5 mm in length, and 0.2 mm in width).^[7,8] The effective illuminated area was controlled to 36.4 mm². I–V measurement was done using a Keithley 4200 source meter. The photoresponse characteristics for the photodetector were collected by a Keithley 4200 source meter with a 532 nm wavelength laser. All above measurements were carried out at room temperature.

Supplementary Data

Figure S1. The photos of BA_2PbI_4 before and after induced by MA gas. (d) The change process of powder XRD patterns for the BA_2PbI_4 .

Figure S2. In situ optical microscope observation of the transformation of BA₂PbI₄ to

 $(MA_{0.32}BA_{0.68})_2PbI_4$ induced by methylamine gas.

Figure S3. The photos of the hybrid perovskite before and after the induced of methylamine (CH₃NH₂) gas. (BA= Butylamine = $C_4H_9NH_3$, HA = Hexylamine = $C_6H_{13}NH_3$, DMA= Dimethylamine=NH₂(CH₃)₂, OA= Octylamine = $C_8H_{17}NH_3$, GA= Guanidine = CH₅N₃).

Figure S4. The powder XRD patterns for the transformational $DMAPbI_3$ after exposed to air for 15 days.

Figure S5. (a) FT-IR spectroscopic analysis of DMAPbI₃ and $MA_{0.2}DMA_{0.8}PbI_3$. (b) 1H-NMR spectrum of $MA_{0.2}DMA_{0.8}PbI_3$. (c) 13C-NMR spectrum of $MA_{0.2}DMA_{0.8}PbI_3$.

Figure S6. (a) FT-IR spectroscopic analysis of BA_2PbI_4 and $(MA_{0.32}BA_{68})_2PbI_4$. (b) 1H-NMR spectrum of $(MA_{0.32}BA_{68})_2PbI_4$. (c) 13C-NMR spectrum of $(MA_{0.32}BA_{68})_2PbI_4$.

Figure S7. (a) Powder photographs of MAPbI₃ with DMAPbI₃ with different molar ratio. (b) UV-vis diffuses reflectance spectroscopy of the above mixture. (c) UV-vis diffuses reflectance spectroscopy of DMAPbI₃ induced by MA gas for 24 h and MAPbI₃. (d) PL spectroscopy of MA_{0.2}DMA_{0.8}PbI₃ from 350 nm to 900 nm.

Figure S8. (a, b) Steady-state absorption and photoluminescence of BA_2PbI_4 and $(MA_{0.66}BA_{0.34})_2PbI_4$ single crystal. Insets: corresponding Tauc plots displaying the extrapolated optical band gaps. (c, d) transient absorption of BA_2PbI_4 and $(MA_{0.32}BA_{0.68})_2PbI_4$ single crystal.

Table S1. Crystal data and structure refinement of $DAPbI_3$ before and after the induced by MA gas for 24 h and 10 days.



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Empirical formula	DMAPbI ₃ ^a	$MA_{0.2}DMA_{0.8}PbI_{3}{}^{b}$	MAPbI ₃ ^c
Formula weight/ g·mol ⁻¹	631.93	631.93	619.91
Temperature/K	273	296	296
Wavelength/ Å		0.71073	
Crystal color		black	
Crystal system	Hexagonal	Hexagonal	Cubic
Space group	P63/mmc	P63/mmc	Pm-3m
a/Å	8.778(2)	8.749(12)	6.3026(13)
b/Å	8.778(2)	8.749(12)	6.3026(13)
c/Å	8.212(2)	8.206(11)	6.3026(13)
$\alpha/^{\circ}$	90	90	90
β/°	90	90	90
$\gamma/^{\circ}$	120	90	90
Volume/Å ³	547.9(2)	543.98(13)	250.36
Crystal size (mm^3)	$0.6\times0.1\times0.1$	$0.69 \times 0.14 \times 0.12$	0.22×0.18×0.06
Ζ	2	2	1
Density/g·cm ⁻³	3.830	3.821	3.992
$\mu(\text{mm}^{-1})$	23.771	23.947	26.007
F (000)	520	520	248
Theta range (data collection)	2.68 to 25.99	2.69 to 24.97	3.23 to 27.26
	-10<=h<=10	-10<=h<=10	-8<=h<=5
Limiting indices	-10<=k<=10,	-10<=k<=10,	-8<=k<=8,
	- 10<=l<=8	-9<=]<=9	- 8<=1<=7
Reflections	2833/233 [R(int)	4989/212 [R(int)	1387/85 [R(int)
collected / unique	= 0.0621]	=0.0391]	= 0.0684]
GOF on F ²	1.086	1.100	1.059
Absorption correction	Semi-empirical from equivalents		
Data / restraints / parameters	233/0/15	212 /0 / 15	85/0/6
$R_{1}, wR_{1} [I > 2\sigma (I)]$	0.0441, 0.1142	0.0244, 0.0688	0.0387, 0.1208
R_2 , w R_2 (all data)	0.0451, 0.1155	0.0249, 0.0692	0.0387, 0.1208
$w_a = 1/[s^2(Fo^2) + (0.0863P)^2 + 1.1140P]$ where $P = (Fo^2 + 2Fc^2)/3$;			
$w_b = 1/[s^2(Fo^2) + (0.0380P)^2 + 3.0548P]$ where $P = (Fo^2 + 2Fc^2)/3$;			

 $w_c = 1/[s^2(Fo^2) + (0.0875P)^2 + 2.6257P]$ where $P = (Fo^2 + 2Fc^2)/3$.

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