# Supporting Information

## Controlled Crystal Orientation and Reduced Lattice Distortion with Cystamine Dihydrochloride Spacer for Efficient and Stable 2D/3D Perovskite Solar Cells

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***Experimental Section***

***Materials and Reagents:*** N, N-dimethylformamide (DMF, 99.8% purity), dimethyl sulfoxide (DMSO, 99.9% purity), acetonitrile (99.8% purity), chlorobenzene (CB, 99.8% purity), 4-tert-butylpyridine (tBP) were purchased from SigmaAldrich and used as received without further purification. Lead iodide ($PbI_2$, 99.999%), tin (IV) oxide ($SnO_2$, 15% in $H_2O$ colloidaldispersion liquid) and lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI, >98%) were purchased from Alfa Asear. Cystamine dihydrochloride (CysCl, 96% purity) was purchased from Merck KGaA. Formamidinium iodide (FAI, 99.8%), methylamine iodide (MAI,99.5%) and methylamine hydrochloride (MACl, 99.5%) were purchased from Xi'an Yuri Solar Co., Ltd. Lead iodide ($PbI_2$,99.9985% purity) and 2,2',7,7'-Tetrakis [N, N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-OMeTAD, 99% purity) were purchased from Advanced Election Technology Co., Ltd. Indium tin oxide (ITO) (transmission>95%) substrates were purchased from South China Science & Technology Company Limited. Unless specified, all chemicals are employed as received without further modifications after purchase.

***Device Fabrication:*** Indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonic treatment in detergent, deionized water and isopropyl alcohol for 20 min and then dried with a nitrogen stream. Then the substrates were treated with UV-ozone for 20 min in plasma cleaner. $SnO_2$ colloidal solution was spin-coated on ITO at 3000 rpm for 30 s, and then annealed at 150 °C for 30 min in air. Then the substrates were treated with UV-ozone for 10min in plasma cleaner to improve the surface wetting before next step. Perovskite active layers were fabricated by two-step interdiffusion process, where 1.5 M of $PbI_2$ in DMF:DMSO (v/v 900/100) solvent containing CysCl additive with different concentrations (0.5, 1 and 1.5 mg/mL) was spin-coated onto $SnO_2$ layer and annealed at 70 ℃ for 1min. Then, a solution of FAI: MAI: MACl (90 mg: 6.9 mg: 9 mg in 1ml IPA) was spin-coated onto the $PbI_2$ at 2000 rpm for 30 s, and the perovskite precursor film was taken out from the nitrogen glove box to ambient air for thermal annealing at 150 °C for 15 min in humidity

conditions (30-40% humidity). After the substrates cooled to room temperature, the spiro-OMeTAD solution was prepared by adding 72.3 mg spiro-OMeTAD in the solvent (CB 1 mL, 4-tertbutylpyridine 28.8 μL, Li-TFSI acetonitrile solution 17.5 μL, 520 mg $mL^{-1}$). Finally, a 100 nm Ag anode was deposited by thermal evaporation (rate of 1.0 Å $s^{-1}$) using a metal shadow mask. The device area was 0.04 $cm^2$. All devices' measurements were carried out in drying cabinet at room temperature.

***Characterizations:*** Keithley 2400 was used to characterize the current density-voltage (*J-V*) curves. The currents were measured under 100 $mW \cdot cm^{-2}$ simulated AM 1.5 G irradiation (Abet5 Solar Simulator Sun2000). The standard silicon solar cell was corrected from NREL and the currents were detected under the solar simulator (Enli Tech, 100 mW $cm^{-2}$, AM 1.5 G irradiation). The forward scan range is from 0 V to 1.22 V and the reverse scan range is from 1.22 V to 0 V, with 20 mV for each step. The scan rate for the *J-V* measurement is 0.2 V/s. Devices were stored and tested in the nitrogen-filled glovebox. Scanning electron microscopy (SEM) was conducted on SU8020 scanning electron microscope operated at an acceleration voltage of 5 kV. Atomic force microscopy (AFM) images were measured by MultiMode 8- HR (Bruker) atomic force microscope. X-ray diffraction (XRD) spectra were carried out by using X-ray diffractometer (Bruker D8Discover 25). The ultraviolet-visible (UV-vis) spectra were characterized on UV-2600 spectrophotometer (Agilent Technologies Inc. Cary 5000 spectrophotometer). The Fourier-transform infrared (FTIR) spectra were conducted on Shimadzu IRAffinity-1S and Thermo Scientific Nicolet iS20. The steady-state photoluminescence (PL) spectra were recorded by fluorescence spectrophotometer (Hitachi F-7000) and time-resolved photoluminescence (TRPL) spectra were recorded by an Edinburgh instruments FLS920 spectrometer (Edinburgh Instruments Ltd.). The PL mapping images were conducted by FastFLIM Q2 (ISS Inc.). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was used for binding energy and element distribution analysis. The water contact angle has been recorded at a Krüss DSA100s drop shape analyzer. External quantum efficiency (EQE) values

were measured under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with an Oriel 70613NS QTH lamp), and the calibration of the incident light was performed using a monocrystalline silicon diode. Electrical impedance spectroscopy (EIS) of the devices was performed in a frequency range from 1 MHz to 10 MHz using Zahner electrochemical workstation at an applied bias equivalent to the open-circuit voltage of the cell under 1 sun illumination.

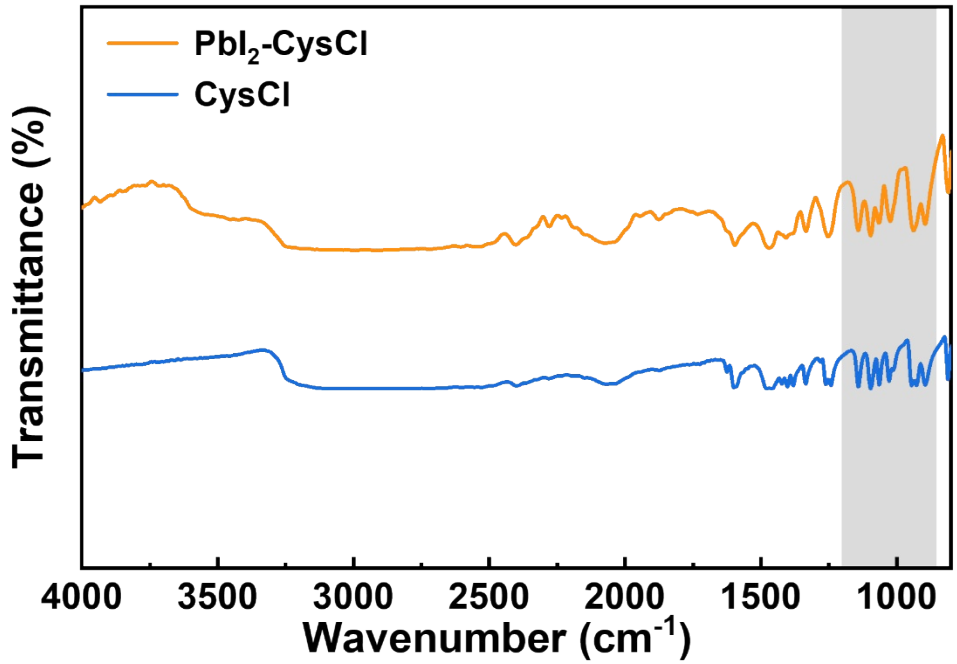


**Fig. S1**. Fourier transform infrared spectrometer (FTIR) spectra of $PbI_2$ film and $PbI_2$ film with CysCl.

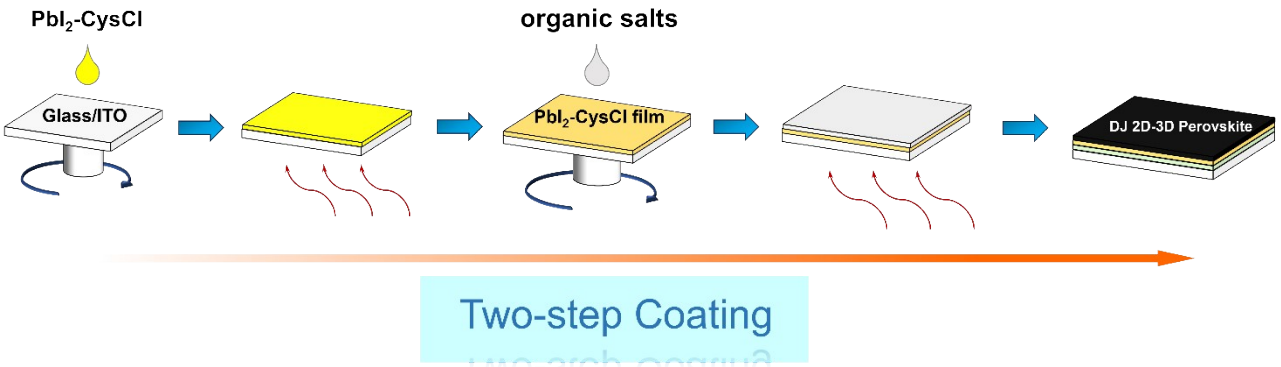


**Fig. S2**. Schematic of preparing 2D/3D perovskite by two-step preparation process.

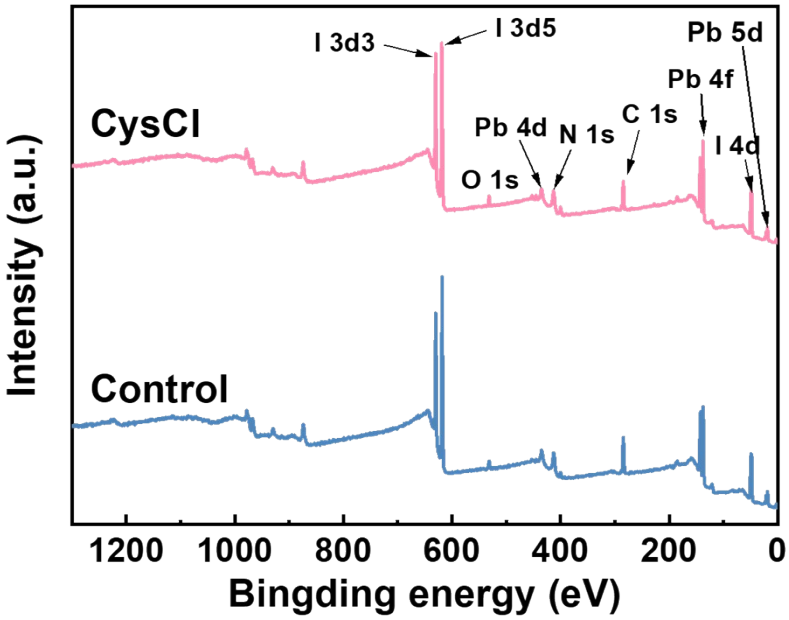


**Fig. S3.** X-ray photoelectron spectroscopy (XPS) of full scan for pure 3D perovskite and 2D/3D perovskite with CysCl.

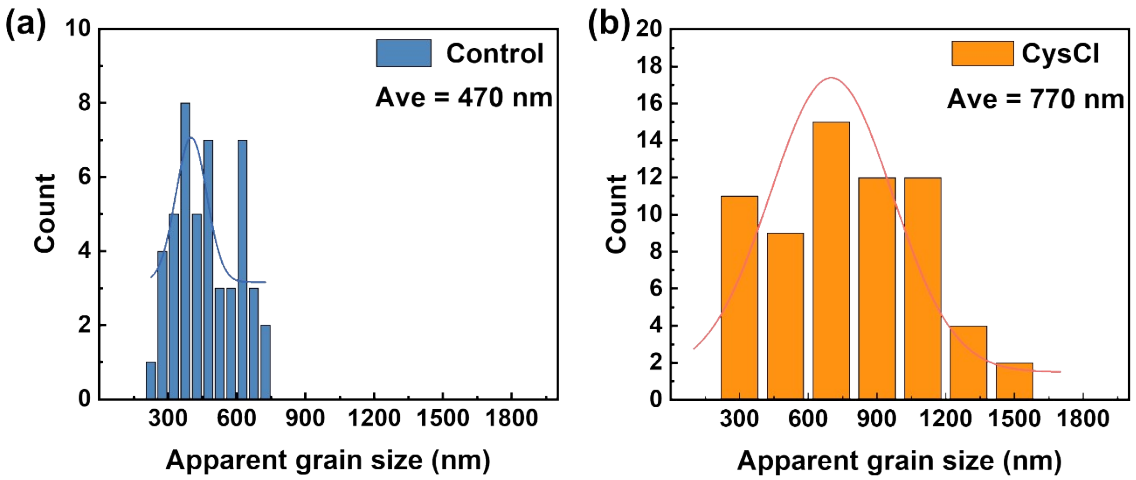


**Fig. S4**. Apparent grain size distributions calculated from top-view SEM images of control and perovskite films with CysCl using the Nanomeasurer 1.2 software.

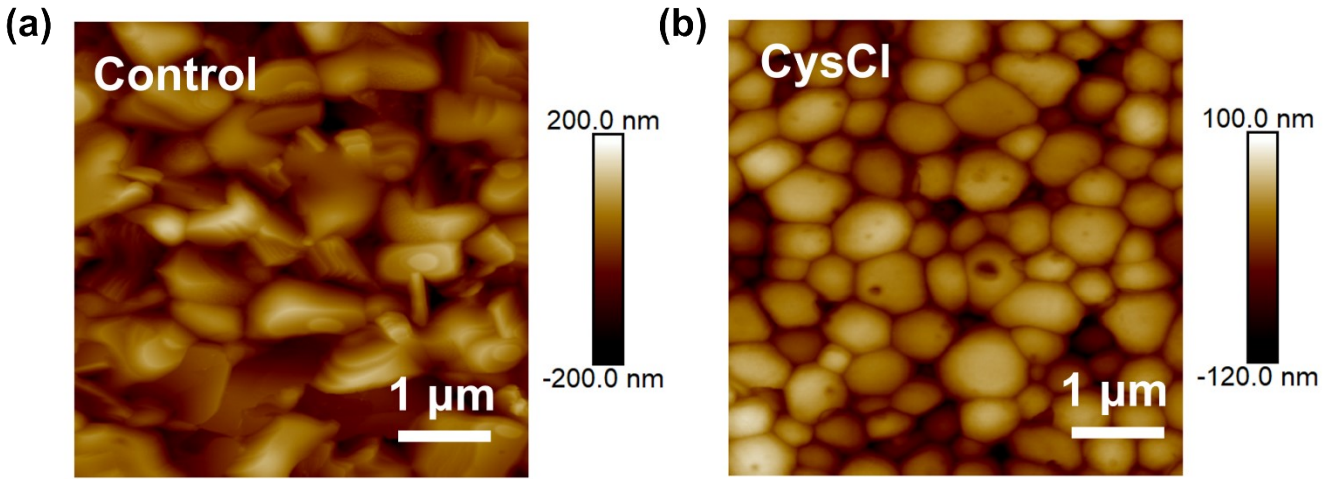


**Fig. S5.** Atomic force microscope (AFM) images of (**a**) pure 3D perovskite and (**b**) 2D/3D perovskite with CysCl.

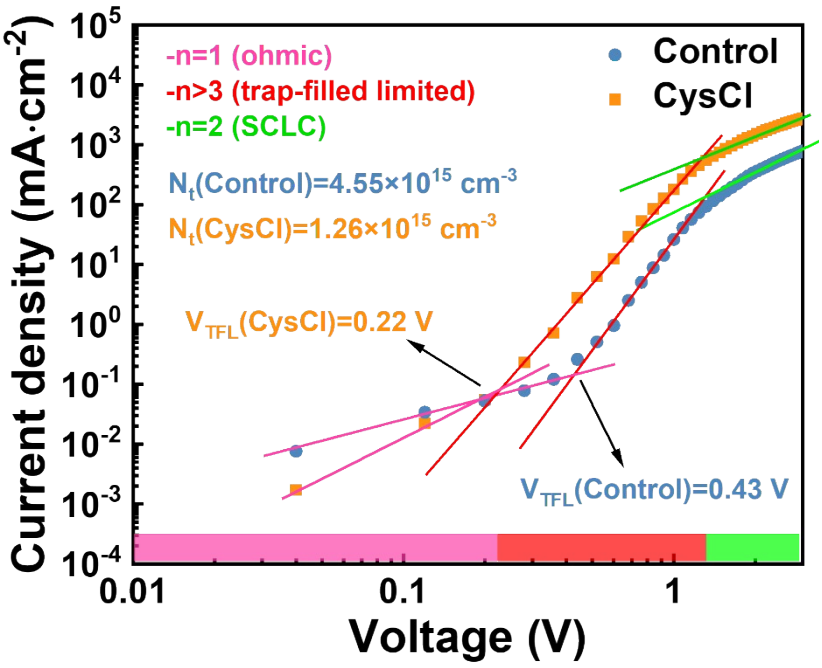


**Figure S6.** Current-voltage (*J-V*) curves for the electron-only devices with structure of ITO/$SnO_2$/Perovskite (pure 3D and CysCl-incorporated 2D/3D)/spiro-OMeTAD/Ag based on the space-charge-limited-current (SCLC) model.

The trap density (*Nt*) was calculated using the following formula:

$$N_t = \frac{2\varepsilon_0\varepsilon_r V_{TFL}}{qL^2}$$

where $q$ denotes the elementary charge of electron, $L$ denotes the thickness of the deposited perovskite layer, $\varepsilon_0$ denotes the vacuum permittivity (8.85 × $10^{-12}$ F·$m^{-1}$), $V_{TFL}$ is the starting voltage of the trap-filled limit area and $\varepsilon_0$ denotes the relative dielectric constant (46.9). The calculated trap density ($N_t$) for CysCl-incorporated 2D/3D perovskite is 1.26 × $10^{15}$ $cm^{-3}$, which is lower than that of pure 3D perovskite (4.55 × $10^{15}$ $cm^{-3}$). The results of SCLC demonstrate that the introduction of CysCl can effectively passivate defects.

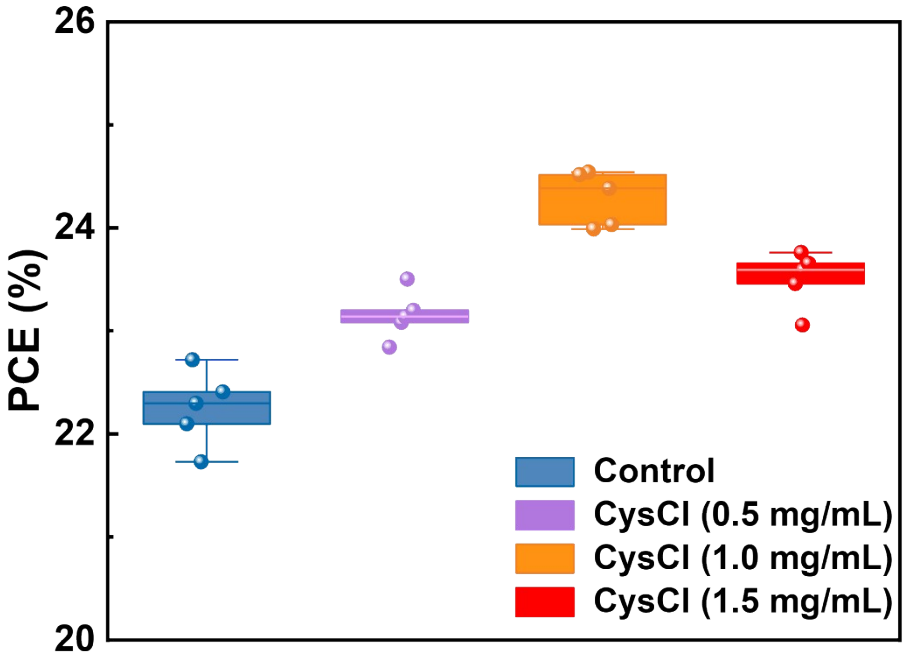


**Figure S7.** Distribution scatter plots of PCE with different concentrations of addition.

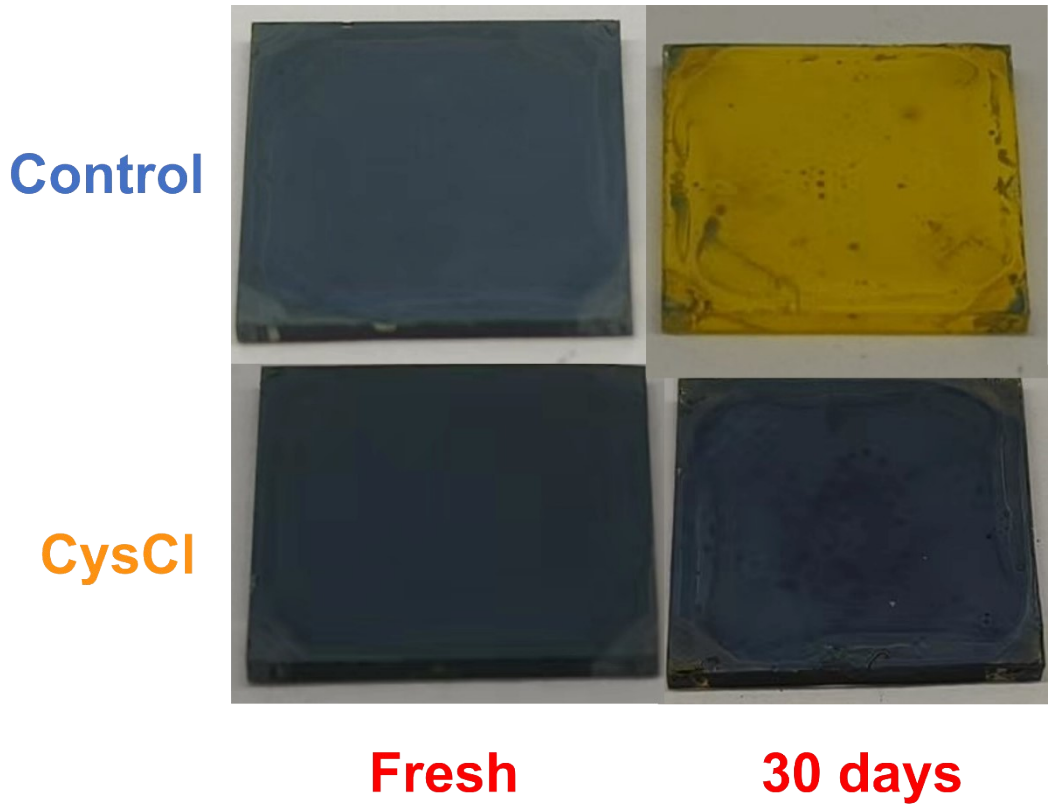


**Fig. S8**. The optical images of pure 3D perovskite and 2D/3D perovskite films with Cyscl upon different exposure durations (fresh and 30 days) in air with 75±5% RH.

**Table S1**. The parameters of time-resolved photoluminescence measurement of pure 3D and 2D/3D perovskite films with CysCl.

| Sample | $\tau_1$ (ns) | $\tau_2$ (ns) | A | $B_1$ | $B_2$ | $\tau_{ave}$ (ns) |
|---|---|---|---|---|---|---|
| **Control** | 61.0 | 136.1 | 388.9 | 3066.7 | 1432.0 | 84.9 |
| **CysCl** | 90.8 | 73.8 | 104.37 | 1556.8 | 5276.7 | 590.7 |

**Table S2.** Summary of the simulation parameters for PVSCs based on pure 3D perovskite and 2D/3D perovskite layers with CysCl.

| Device | $R_{ct}$ (Ω) | $R_{rec}$ (Ω) |
|---|---|---|
| **Control** | 185.6 | $1.0\times10^4$ |
| **CysCl** | 121.0 | $3.0\times10^4$ |