Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Study on the long time aging behavior for $MAPbI_3$: From experimental to first-principle simulation

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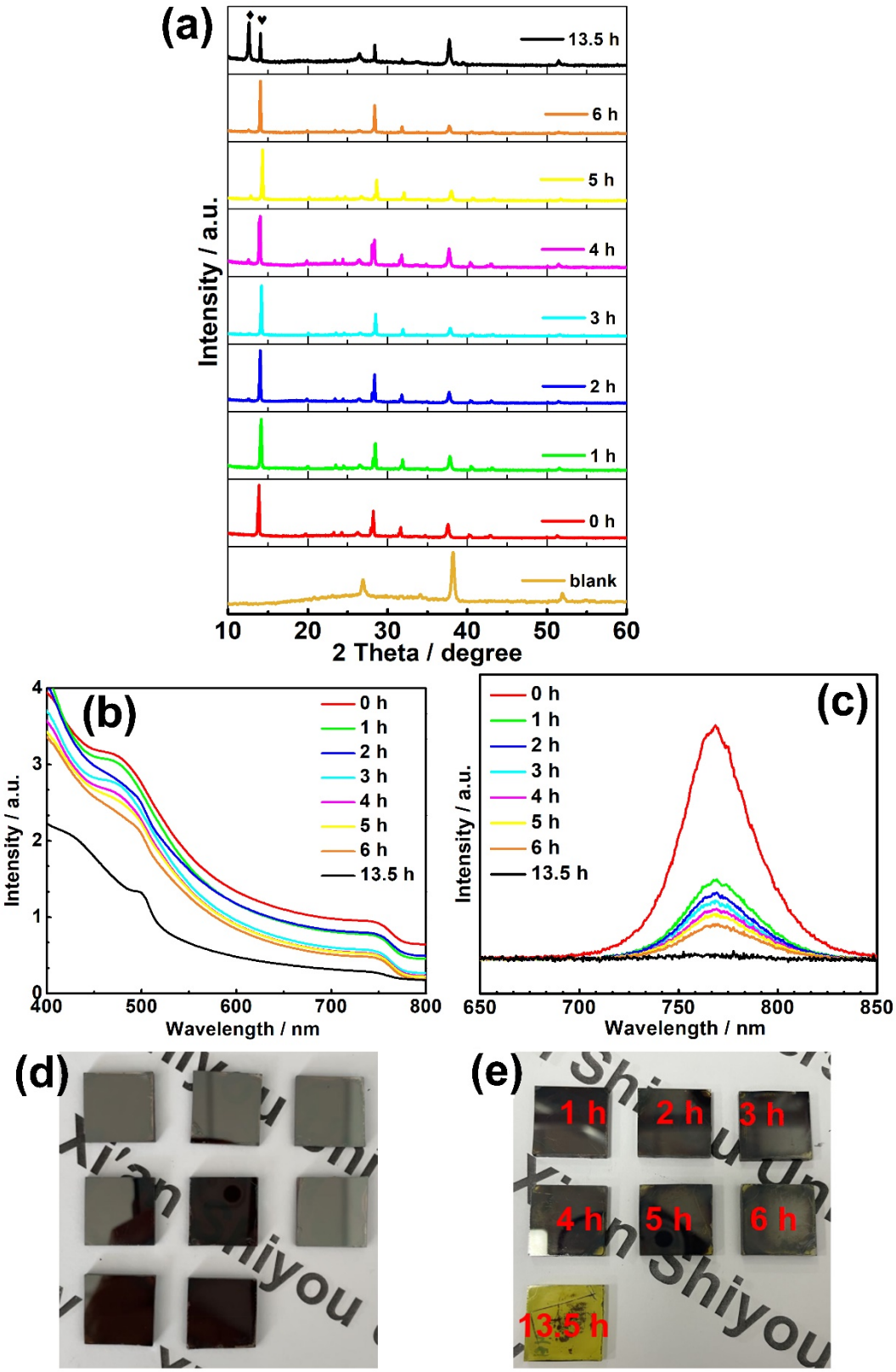

Fig. S1 $MAPbI_3$ films aged by AM1.5 illumination in atmospheric environment: (a) XRD patterns, (b) UV-vis absorption spectra, (c) steady-state PL spectra and (d) photos before aging and (e) after aging for 6 hs, where ♥is the (110) of $MAPbI_3$ and ♦ (001) of the PbI_2

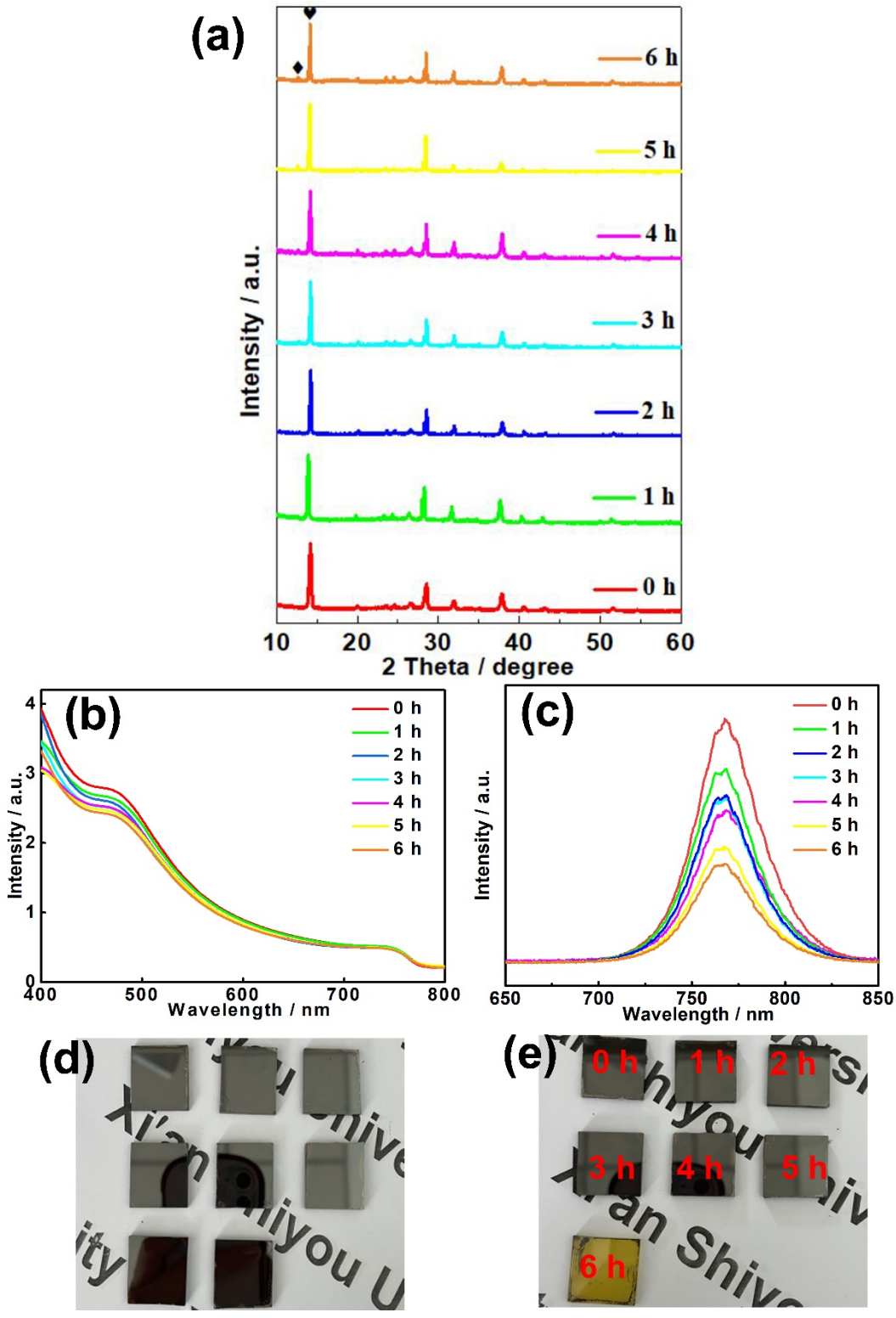

Fig. S2 $MAPbI_3$ film aged by AM1.5 illumination at N_2 environment: (a) XRD patterns, (b) UV-vis absorption spectra, (c) steady-state PL spectra and (d) photos before aging and (e) after aging for 6 hs, where ♥is the (110) of $MAPbI_3$ and ♦ (001) of the PbI_2.

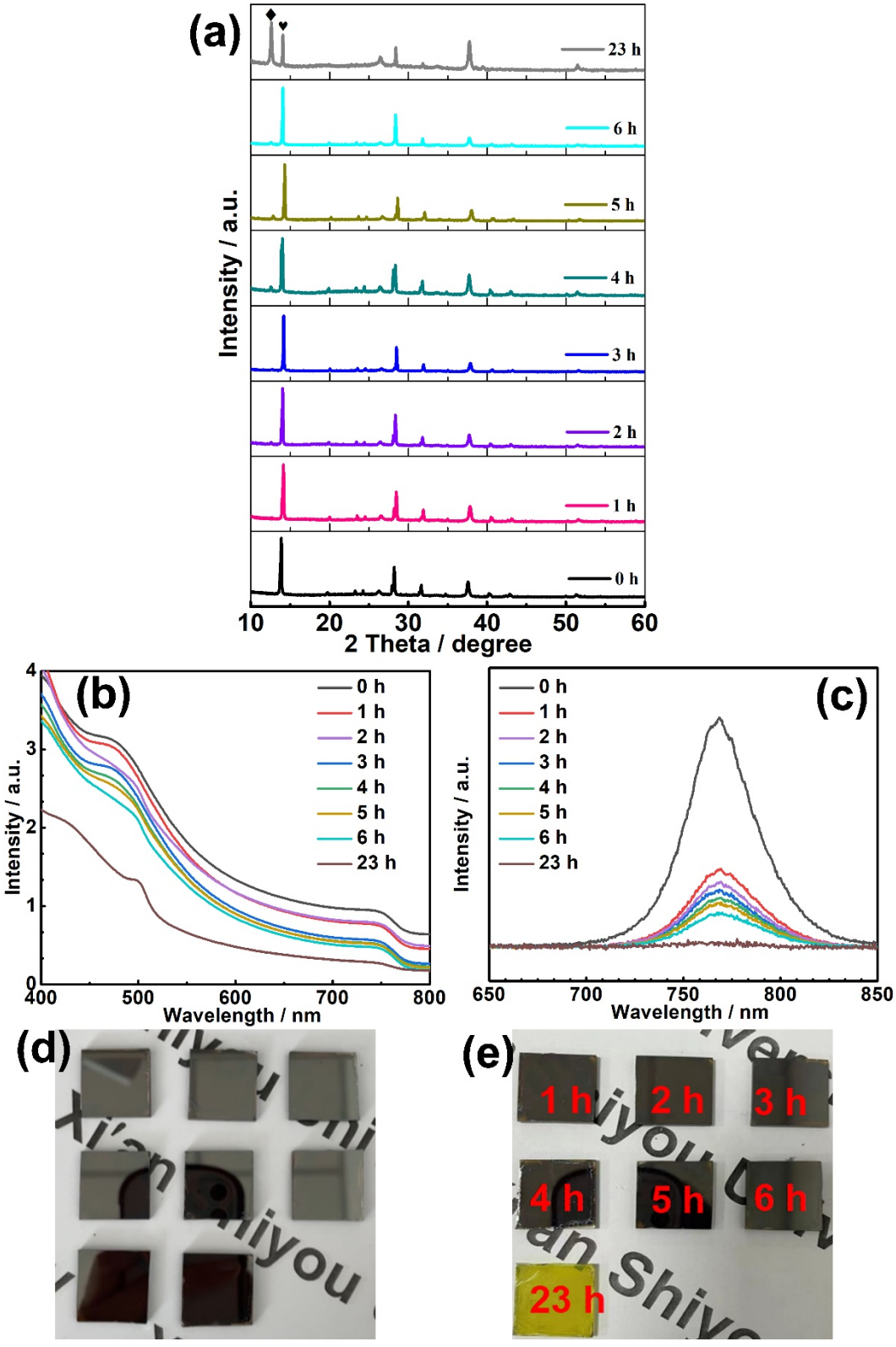

Fig. S3 $MAPbI_3$ film aged by ultraviolet light in atmospheric environment: (a) XRD patterns, (b) UV-vis absorption spectra, (c) steady-state PL spectra and (d) photos before aging and (e) after aging for 6 hs, where ♥is the (110) of $MAPbI_3$ and ♦ (001) of the PbI_2.

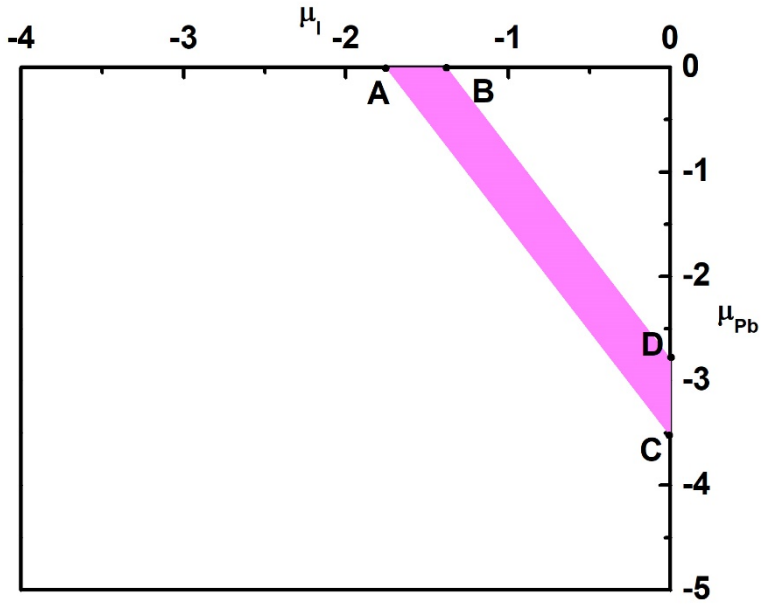

Fig. S4 The phase diagram of the stable $MAPbI_3$.

Table. S1 The total energies of possible competitive phases.

System	Energy (eV)	System	Energy (eV)
I_2(gas)	-2.657	C (graphite)	-9.309
Pb(metal)	-3.806	N_2(molecule)	-8.314
MAI(solid phase)	-42.797	H_2(molecule)	-3.383
PbI_2(solid phase)	-9.2539	MA	-37.92
$MAPbI_3$	-52.019		

Table S2 The element chemical potential under different chemical conditions in the stable $MAPbI_3$ phase.

I-poor/Pb-rich	I-rich/Pb-poor
Point A	**Point C**
μ_{Pb}=0 eV	μ_{Pb}=-3.52 eV
μ_I=-1.76 eV	μ_I=0 eV
μ_{MA}=-1.03 eV	μ_{MA}=-2.79 eV

In the calculated surface defect properties of $MAPbI_3$, the defect formation energies and defect energy levels of different surface defects were calculated to

identify types of surface deep level defects. The types of surface defects include vacancies (V_{MA}, V_{Pb}, V_I), interstitials (MA_i, Pb_i, I_i) and anti-site substitutions (MA_I, I_{MA}, Pb_I, I_{Pb}, MA_{Pb}, Pb_{MA}, A_B means A on B site).

Defect formation energies were calculated by $\Delta H = E_D - E_P - \sum_i n_i(\mu_i + \mu_j)$.Where E_D and E_P are the energies of slab containing defect and prefect, n_i represents the lose atom (+) or surplus atom (-) number, μ_i and μ_j are their chemical potential, which can be expressed as $\mu_i = \Delta\mu_i + \mu_i^{solid}$, μ_i^{solid} is the chemical potential of the relevant elemental solid. The defect formation energy is related to the constituent element. The chemical potentials of different conditions and stable $MAPbI_3$ without the formation of other competing phases can be obtained from the phase diagram meeting the following conditions

$$\mu_{MA} + \mu_I < \Delta H(MAI) = -3.55eV \quad \text{eqn.S1}$$

$$\mu_{Pb} + 2\mu_I < \Delta H(PbI_2) = -2.79eV \quad \text{eqn.S2}$$

$$\mu_{MA} + \mu_{Pb} + 3\mu_I = \Delta H(MAPbI_3) = -6.31eV \quad \text{eqn.S3}$$

$$\mu_{MA} < 0 \quad \text{eqn.S4}$$

$$\mu_{Pb} < 0 \quad \text{eqn.S5}$$

$$\mu_I < 0 \quad \text{eqn.S6}$$

Where $\Delta\mu_{MA}$, $\Delta\mu_{Pb}$, $\Delta\mu_I$ are the chemical potentials of MA, Pb, I and Br, respectively, ΔH(MAI), $\Delta H(PbI_2)$ and $\Delta H(MAPbI_3)$ are the formation enthalpies of MAI, PbI_2 and $MAPbI_3$, respectively.