Hydrogenated Cs2AgBiBr6 for High-Efficient Lead-Free Inorganic Double Perovskite Solar Cell

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**Supplementary Figure 1.** **X-ray diffraction (XRD) patterns of Cs2AgBiBr6 perovskite films with different hydrogenation time of 0 s, 1,800 s, 2,400 s and 3,000 s.** **Cs, Ag, Bi and Br atoms are represented by cyan, light grey, purple and brown dots, respectively.** The XRD peaks of all films are identified as the cubic phase () Cs2AgBiBr6 (the host standard crystal structure as shown in inset figure). However, the intensity of the XRD peaks decrease as the increase of hydrogenation time, which may be related to the reduction of the crystallinity in Cs2AgBiBr6 causing by hydrogenation. As the increase of hydrogenation time up to 1,800 s or longer, an additional XRD peak of CsBr (110) appeared, indicating a phase transition in the hydrogenated Cs2AgBiBr6 films.



**Supplementary Figure 2.** **Tauc plots of the Cs2AgBiBr6 perovskite films with different hydrogenation time, which is calculated through the direct bandgap method.** However, the direct bandgap value of hydrogenated 1,200 s Cs2AgBiBr6 perovskite film is calculated to be 1.96 eV, which is not suitable for the black color of hydrogenated Cs2AgBiBr6 perovskite film. Thus, the Cs2AgBiBr6 perovskite film after hydrogenation is still an indirect bandgap material.



**Supplementary Figure 3. (a)** The hall coefficient (*RHAν*) and (**b)** specific resistance of the Cs2AgBiBr6 perovskite films with different hydrogenation time, which were gained from the hall effect measurement.The carrier mobility was calculated by the equation: Carrier mobility=*RHAν*/Specific Resistance.



**Supplementary Figure 4. Time-resolved photoluminescence (TRPL) of the Cs2AgBiBr6 perovskite films with different hydrogenation time.** After 600 s and 1,200 s hydrogenation treatment, the carrier lifetime of Cs2AgBiBr6 perovskite film increased from 18.85 ns to 30.67 ns and further to 41.86 ns, indicating a proper hydrogenation treatment could improve the transmittability of charge carriers. However, with the further increase of hydrogenation time, the carrier lifetime exhibited a decreasing tendency, which may be caused by the appearance of CsBr impure phase as shown in Supplementary Fig. 1.



**Supplementary Figure 5. (a-e)** The calculated depth-dependent values based on the selected diffusion coefficients from 1×10-15 cm2/s to 1×10-5 cm2/s at the different hydrogenation times (600 s, 1,200 s, 1,800 s, 2,400 s and 3,000 s), respectively. Due to the thickness of Cs2AgBiBr6 film is about 140 nm, then the values at 140 nm for different coefficients were indicated in figures and then summarized in Supplementary Table 3. **(f)** Cross-sectional scanning electron microscope (SEM) image confirms that the Cs2AgBiBr6 film is with a thickness of about 140 nm. **(g)** Schematic diagram presents the depth-dependent H\* concentration distribution in the hydrogenated Cs2AgBiBr6 film. Hydrogen atom is represented by the red dot. *Cs* and *C* represent the hydrogen concentration on the top and bottom surface of hydrogenated Cs2AgBiBr6 film, respectively. Assuming the blackness values of the front and back side images (in Fig. 2a) are respectively proportional to the average H\* concentration near the top and bottom surface of hydrogenated Cs2AgBiBr6 film, as shown by *Csˊ* and *Cˊ*, then the blackness ratio of the back and front side images can be used as the reference ratio of for judging the rationality of the calculated values.



**Supplementary Figure 6. Work function** ***φ*** **of the Cs2AgBiBr6 perovskite films with different hydrogenated time. (a)** 0 s; **(b)** 600 s and **(c)** 1,200 s (insert shows the energy difference *∆E* between *EF* and *EVBM* from the valence band spectra). The energy level of VBM value could be calculated through: *EVBM* =*φ*+*∆E*. Then according to the bandgap value of the hydrogenated Cs2AgBiBr6 perovskite films (Fig. 1), the energy level of CBM value could also be determined.



**Supplementary Figure 7. X-ray photoelectron spectroscopy (XPS) spectra of Br 3d in Cs2AgBiBr6 films with different hydrogenation time (0 s, 600 s and 1,200 s).** The binding energy position of Br 3d in Cs2AgBiBr6 films almost unchanged after 600 s and 1,200 s hydrogenation treatment, which means this may be induced by the coexist of H1(in), H2(in) and H3(in) structures in hydrogenated Cs2AgBiBr6.



**Supplementary Figure 8. (a)** PBE, **(b)** HSE and **(c)** HSE+SOC band structures of host Cs2AgBiBr6 in its primitive cell with the bandgaps of 1.33 eV, 2.23 eV, and 1.98 eV, respectively. As we know, the DFT based on GGA calculations could underestimate the bandgaps of crystalline materials. Here, different kinds of models based on HSE and PBE were used to simulate the band structure of host Cs2AgBiBr6. When compared with the experimental bandgap (2.14 eV) of host Cs2AgBiBr6 (Fig. 1e), it could find that HSE function (2.23 eV) provides more accurate bandgap than PBE function (1.33 eV). Thus, HSE+SOC was adopted to better evaluate the bandgap by considering the relativistic effect of Bi.

**Supplementary Figure 9. The schematic crystal structures and PBE band structures of H\* occupying at three different Br vacancies: (a)** H1 polyhedron and H1(Br), (**b)** H2 polyhedron and H2(Br)r and (**c)** H3 polyhedron and H3(Br) in Cs2AgBiBr6. Cs, Ag, Bi, Br and H atoms are represented by cyan, light grey, purple, brown and red dots, respectively. The band structures show that the three types of Hn(Br) (n=1, 2, 3) have PBE-bandgaps of ~1.30 eV, which is equal to the one in host Cs2AgBiBr6 (Supplementary Fig. 8a). Whereas, experimental observation shows that the bandgap gradually decreased with the increasement of hydrogenation time (Fig. 1e). So, the substitution of H atoms to Br sites are not the main contribution for the optimization of bandgap in hydrogenated Cs2AgBiBr6.



**Supplementary Figure 10. PBE band structures of (a)** pure Cs2AgBiBr6 (host) and **(b-d)** with interstitial H\* including: (**b)** H1(in), **(c)** H2(in**),** and **(d)** H3(in). The band edges for host and interbands for interstitial H\* are highlighted. Red, light green, blue, pink, dark green, and orange curves correspond to Bi 6s, Bi 6p, Ag 4d, Ag 5s, Br 4p and H 1s orbitals, respectively. **(e-h)** The HSE+SOC band structures of Cs2AgBiBr6 (host) and host+interstitial H\* containing H1(in), H2(in), and H3(in). The partially occupied inter bands are marked with blue dots, whose size represent the occupation at different k-points along the high symmetry line. The size of occupation=1 is pointed out for reference. The lower conduction band of the host is predominantly antibonding Bi-6p and Br-4p states, while the upper valence band is the coupling of the Ag-4d orbital with the Br-4p and Bi 6s orbitals. For Hn(in) induced band structures, they are mainly derived from the bonding states of H-1s with nearby cations. In detail, H1(in) would form a wide band which is the coupling of H-1s, Br-4p and Ag-4d, while H2(in) would introduce a narrow one which is the coupling of H-1s, Br-4p and Bi-6p. However, H3(in) form a flat band consisting of H-1s and Br-4p, which was resulted from the H locating at the center of centrosymmetric octahedron.

**Supplementary Table 1. The carrier lifetime of Cs2AgBiBr6 perovskite films with different hydrogenation time.**



**Supplementary Table 2. Summary for the diffusion coefficient of H\* in different materials.**



**Supplementary Table 3. The simulated values as a change of hydrogenation time and H\* diffusion coefficient in the 140 nm thick hydrogenated Cs2AgBiBr6 perovskite films (extracting from the Supplementary Fig. 5).** Here *Cs* is the concentration of hydrogen at the surface of perovskite film, and *C* is the atomic hydrogen concentration at the film depth of 140 nm. Assuming the blackness values of the front and back side images (in Fig. 2a) are respectively proportional to the average H\* concentration near the top and bottom surface of hydrogenated Cs2AgBiBr6 film, as shown by *Csˊ* and *Cˊ*; then the blackness ratio of the back and front side images can be used as the reference ratio of for judging the rationality of the calculated values.

