

Supporting Information

From Particles to Film: Production of Cs₂AgBiBr₆-Based Perovskite Solar Cells and Enhancement of Cell Performance via Ionic Liquid Utilization at the TiO₂/Perovskite Interface

Arzu ÖCEBE¹, İsmail Cihan KAYA^{2,3}*

¹Department of Chemical Engineering, Konya Technical University, Konya, Turkey

²Department of Metallurgical & Materials Engineering, Konya Technical University, Konya, Turkey

³Energy Technologies Research, Development and Application Centre, Konya Technical University, Konya, Turkey

*E-mail address of corresponding author: ickaya@ktun.edu.tr

EXPERIMENTAL SECTION

Synthesis of the Cs₂AgBiBr₆ Particles

Cs₂AgBiBr₆ particles were synthesized by traditional super-saturation precipitation method in ambient atmosphere. Initially, 2 mmol of CsBr (99% Alfa Aesar), 1 mmol of AgBr (99.5% Alfa Aesar), and 1 mmol of BiBr₃ (98% Sigma-Aldrich) were dissolved in 10 mL of HBr (47% aqueous Merck) at 110 °C. The solution was subsequently cooled to 80 °C at a rate of 10 °C per hour and then allowed to naturally cool to room temperature. The resulting orange powder, which precipitated after a day, was collected and subjected to three rounds of washing with ethanol through centrifugation. Finally, the obtained powders were dried under reduced pressure for 5 hours.

Fabrication of the Perovskite Solar Cells

Fluorine-doped tin oxide (FTO) glasses (Sigma Aldrich, 7 Ω/sq) etched with zinc powder and 2 M HCl acid were used as a substrate to fabricate PSCs. Before the deposition of the components of PSCs, the substrates were cleaned with de-ionized water, acetone, ethanol, and treated with UV-ozone, respectively. Initially, Compact TiO₂ (c-TiO₂) and mesoporous TiO₂ (m-TiO₂) layers were deposited by spin coating method as reported our previous study.¹ The perovskite films were deposited on m-TiO₂ film by spin coating at 2000 rpm for 60 s, from the precursor solution containing 0.5 M Cs₂AgBiBr₆ powders in 1 mL dimethylsulphoxide (DMSO). The precursor solution was heated up to 75°C before being dropped onto the substrate. Additionally, 5 seconds after the rotation began during the spin-coating process of the perovskite solution, Ar gas was flowed (flowing rate:18 L/min) over the substrate to remove co-solvents and facilitate perovskite crystallization. The substrates were then annealed at 280 °C for 10 min. on a hotplate. After cooling the films down to room temperature, the devices were completed by carbon electrode (Solaronix, Elcocarb B-L/SP) coating by doctor blade

method and annealed at 100 °C for 30 min. In the process of fabricating the cell with ionic liquids (ILs), BMIMPF₆ was first diluted in isopropanol to attain the desired concentrations of 0.01 wt.%, 0.5 wt.%, and 1 wt.%. Subsequently, this solution was spin-coated onto the m-TiO₂ film, which was annealed at 450 °C, with a spin speed of 4000 rpm for 30 seconds, followed by annealing at 100 °C for 10 minute.

Characterization

The crystal structure and phase distribution of the Cs₂AgBiBr₆ powders and thin films were determined by X-ray diffraction (XRD) analysis. XRD measurements were carried out using a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA with Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The elemental chemical states of all ionic species in the produced samples were examined via high resolution X-ray photoelectron spectroscopy (XPS) analysis using a Thermo Scientific K α X-ray photoelectron spectrometer with monochromatic Al-K α radiation. The absorbance spectra of the films were recorded between 400-850 nm using Shimadzu UV-2600 UV-Vis spectrophotometer. ZEISS GeminiSEM 500 Field Emission Scanning Electron Microscopy (FE-SEM) was used to investigate the microstructural features of the powders and the films. The size distribution of the samples were determined via FE-SEM images employing Image J software. The surface morphology of the TiO₂ films was analyzed using AFM (NT-MDT / Ntegra Solaris). Steady-state and time-resolved PL spectra were measured using an Edinburgh Instruments FLSP920 fluorescence spectrometer with a 400 nm excitation wavelength. The current density-voltage (J-V) curves of the PSCs were recorded using Ossila X200 Source measure unit under Newport Sol1A solar simulator (AM 1.5 G, 100 mW/cm²) at room temperature. The active area of the devices were 0.015 cm².

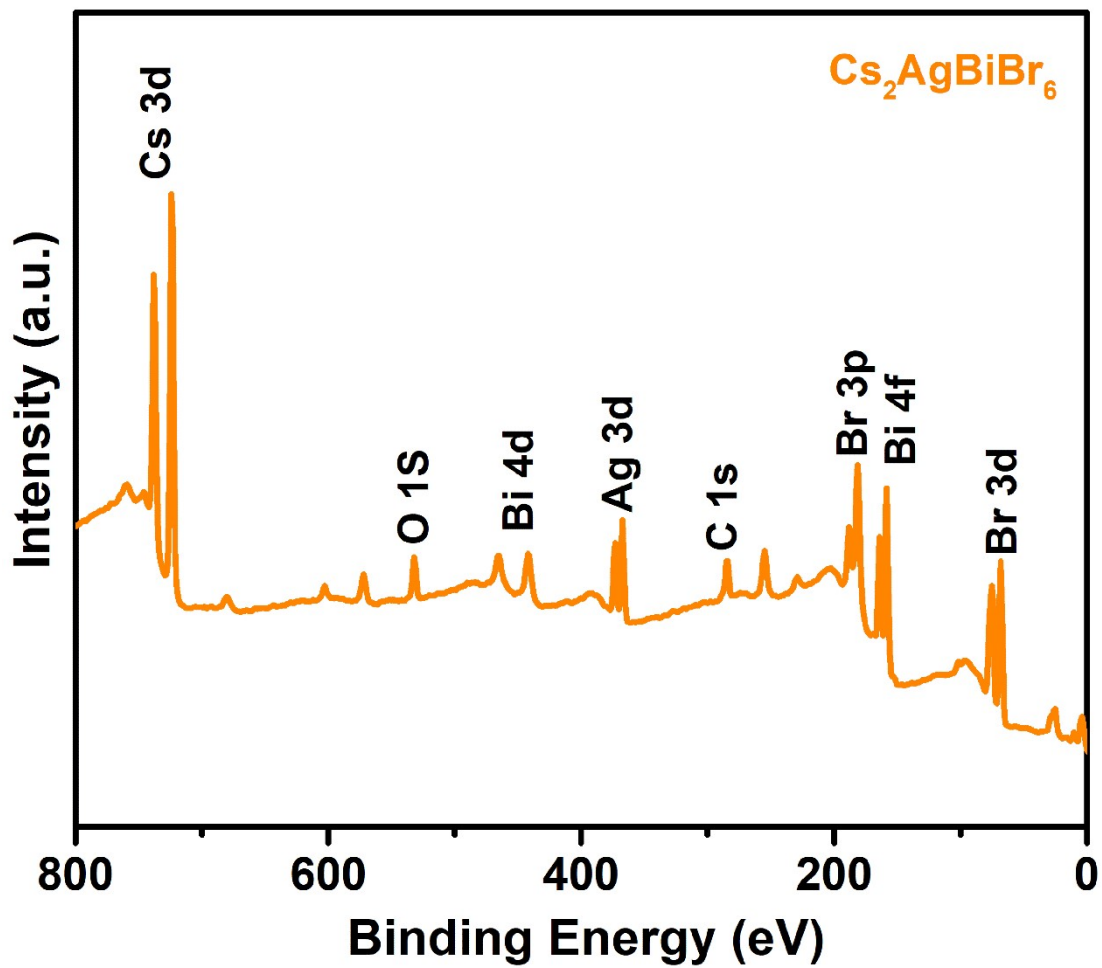


Figure S1. Survey XPS spectrum of the $\text{Cs}_2\text{AgBiBr}_6$ film

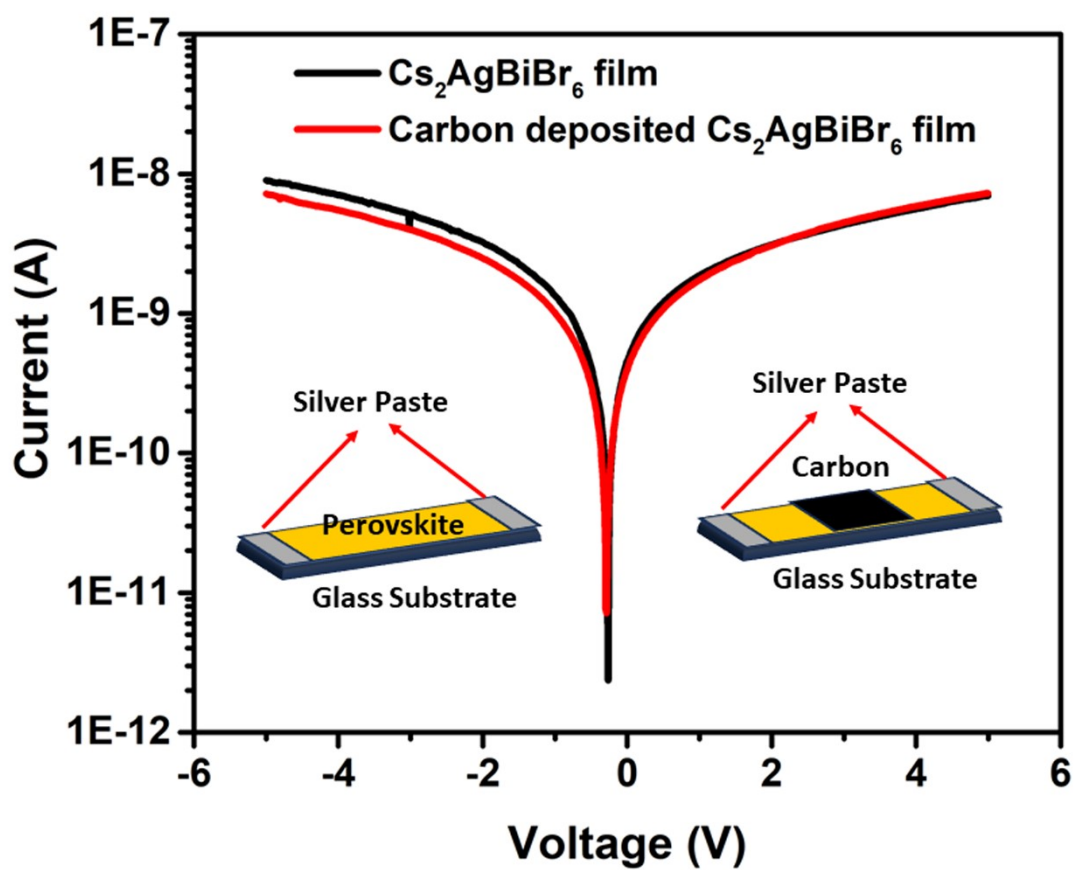


Figure S2. Semi-logarithmic dark I-V measurements of the perovskite samples coated on the glass substrate both before and after the deposition of the carbon electrode.

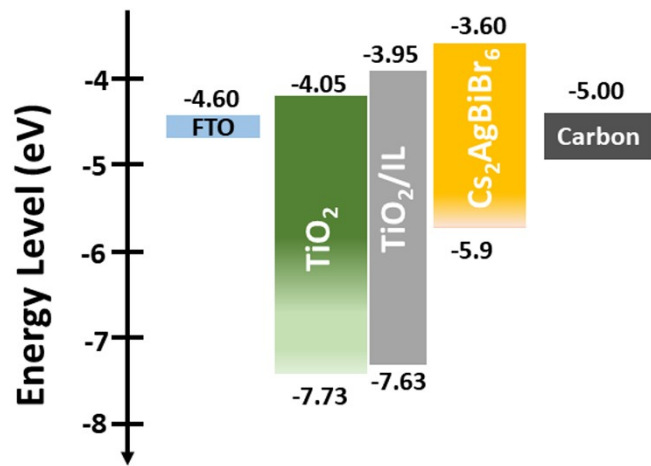


Figure S3. Schematic illustration of the energy level diagram

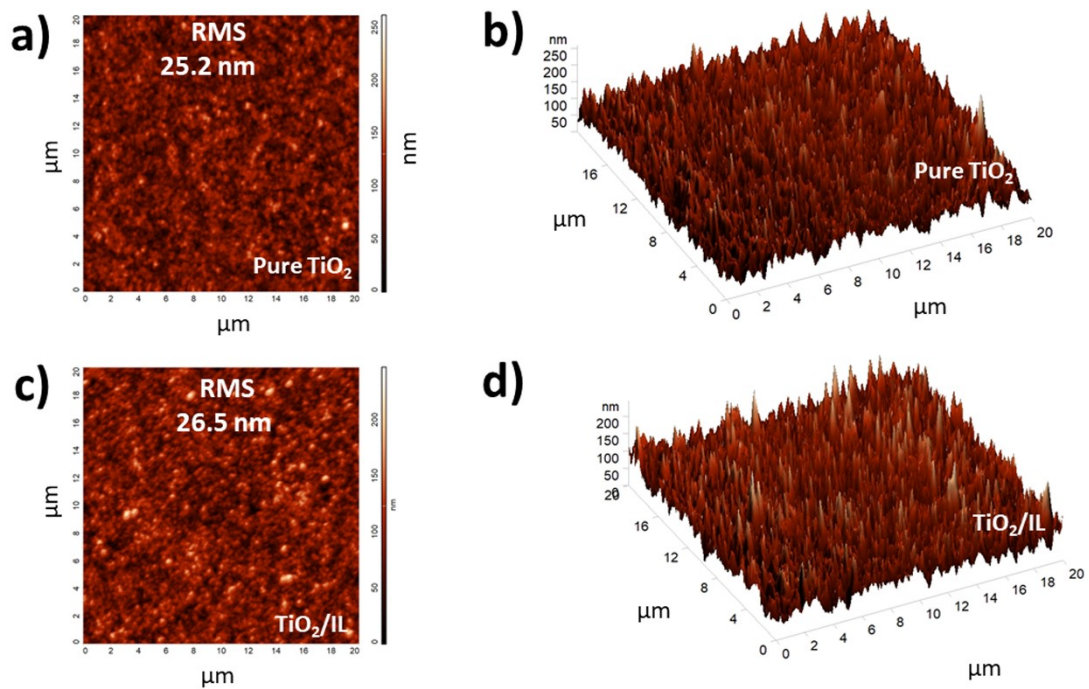


Figure S4. Two and three-dimensional atomic force microscopy (2D and 3D AFM) images of pure and IL modified TiO₂ films

Table S1. Chemical composition of Cs₂AgBiBr₆ thin films and parameters used to calculate composition of film

Elements	Core level	Area	Scofield sensitivity	Composition (at.%)	Atomic ratio
Cs	3d _{5/2}	46266.6	40.22	23.25	1.99
	3d _{3/2}				
Ag	3d _{5/2}	9343.8	18.04	10.47	0.90
	3d _{3/2}				
Bi	4f _{7/2}	14334.4	24.83	11.67	1
	4f _{5/2}				
Br	3d _{5/2}	7676.9	2.84	54.62	4.68
	3d _{3/2}				

1. Öcbe, A.; Deveci, H.; Kaya, İ. C., Gas-Quenching Approach for Fabricating Cs₂AgBiBr₆ Thin Films in Ambient Environment for Lead-Free All-Inorganic Perovskite Solar Cells with Carbon Electrodes. *Energy Technology* n/a (n/a), 2300407.