Supporting Information

UV-Ozone Surface Pretreatment for High Quality ALD-Grown Ultrathin Coatings on Bismuth Oxyhalide Photocatalysts

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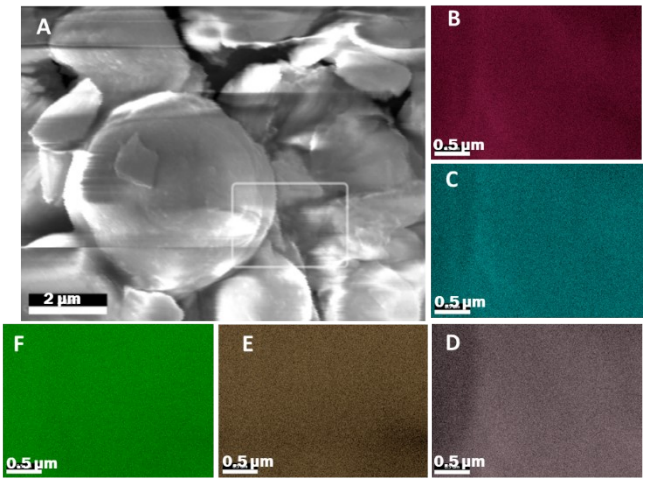


Fig S1 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOCl in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 40^{o}C following UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Cl (F) atoms.

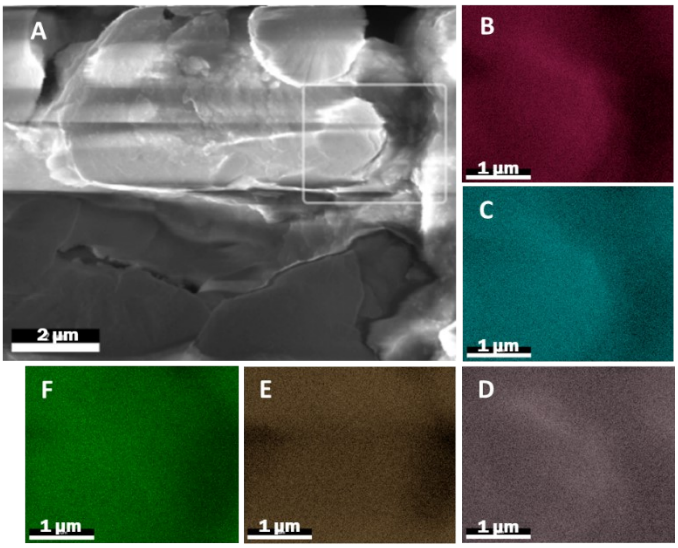


Fig S2 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOCl in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 40^{o}C without UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Cl (F) atoms

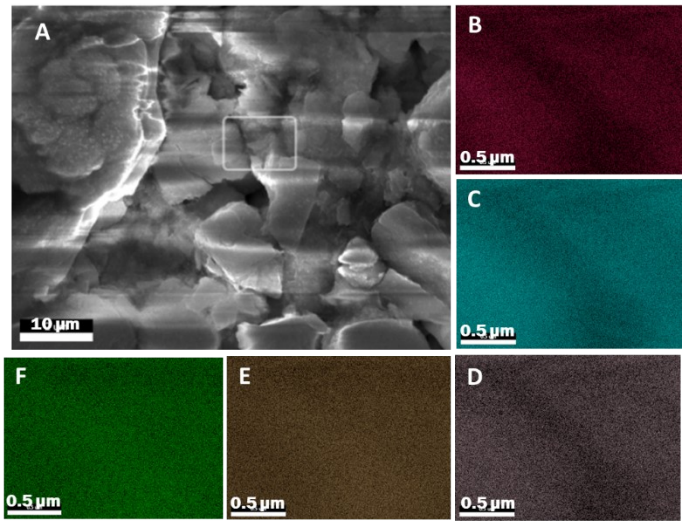


Fig S3 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOBr in an SiO2 binder coated with 10 cycles of Al2O3 ALD at 80^{o}C following UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Br (F) atoms.

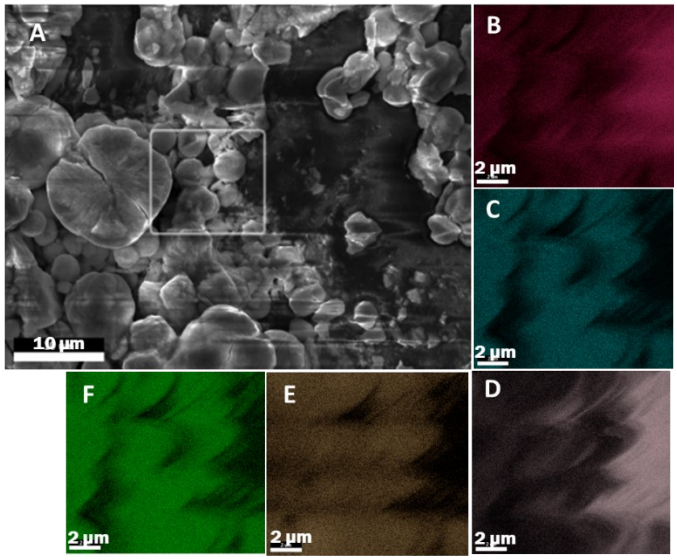


Fig S4 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOBr in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 80^{o}C without UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Br (F) atoms.

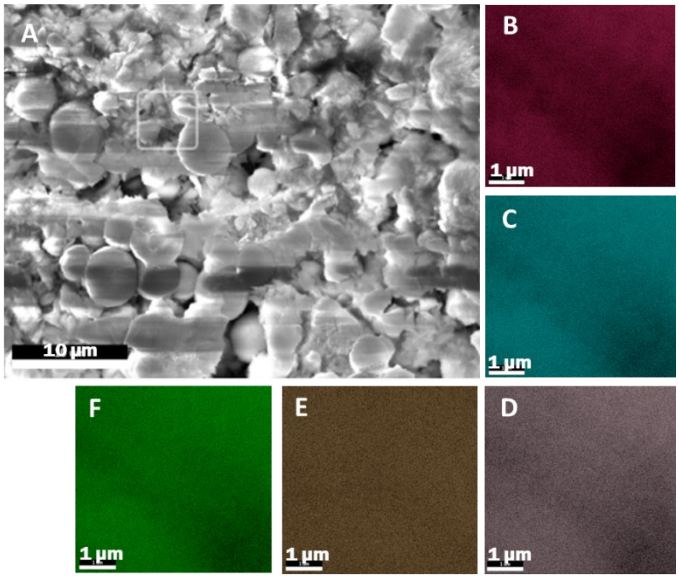


Fig S5 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOBr in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 40°C following UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Br (F) atoms.

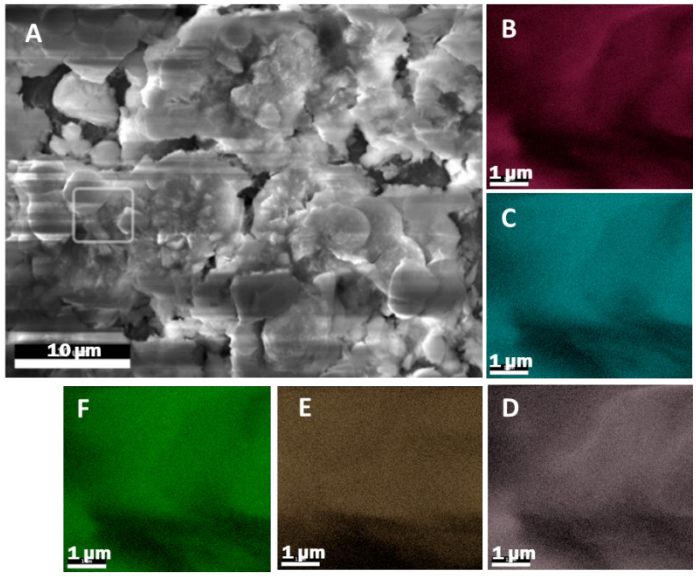


Fig S6 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOBr in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 40°C without UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Br (F) atoms.

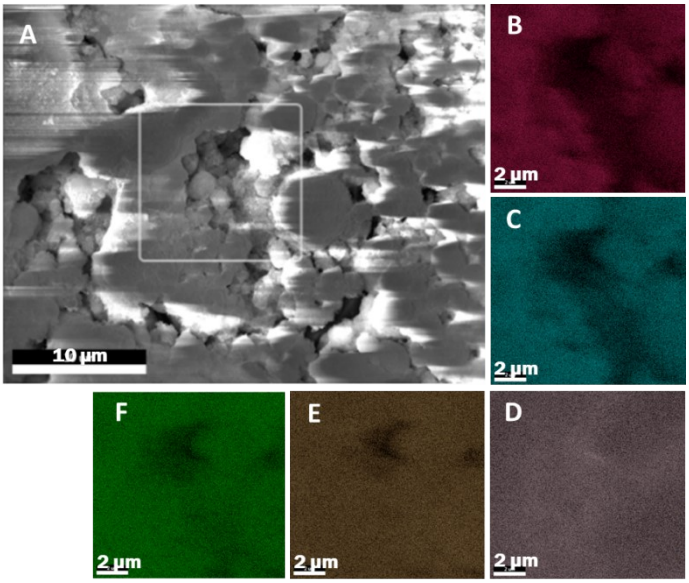
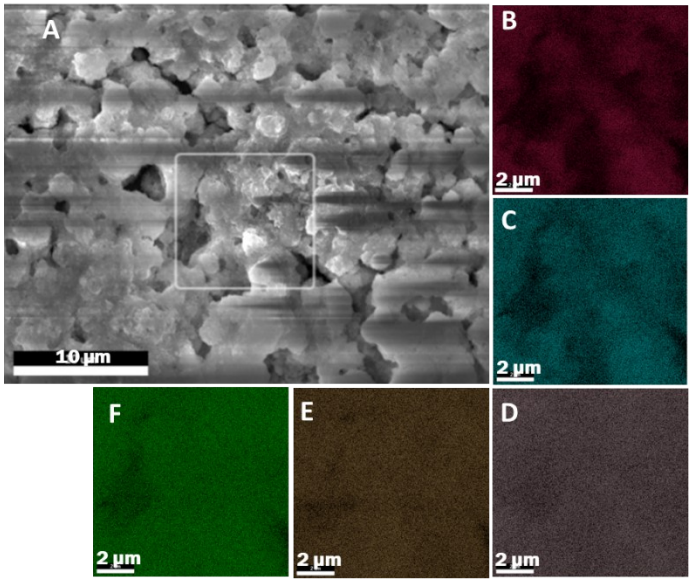


Fig S7 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOI in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 80^oC following UV-ozone



treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and I (F) atoms.

Fig S8 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOI in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 80^oC without UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and I (F) atoms.

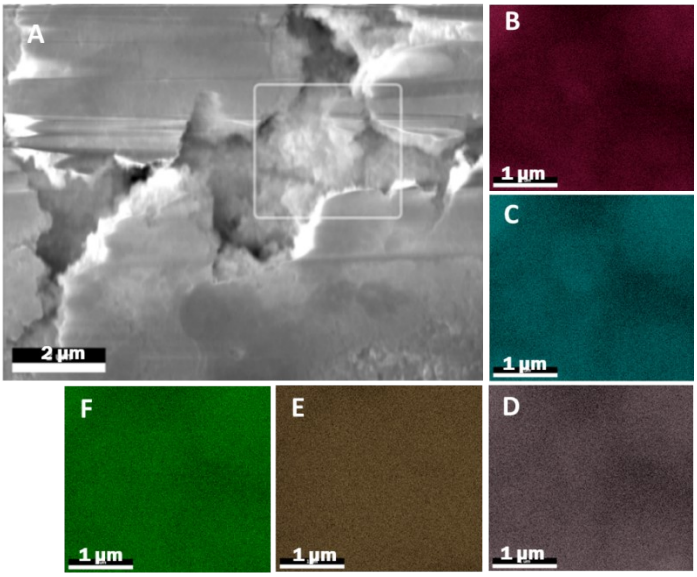
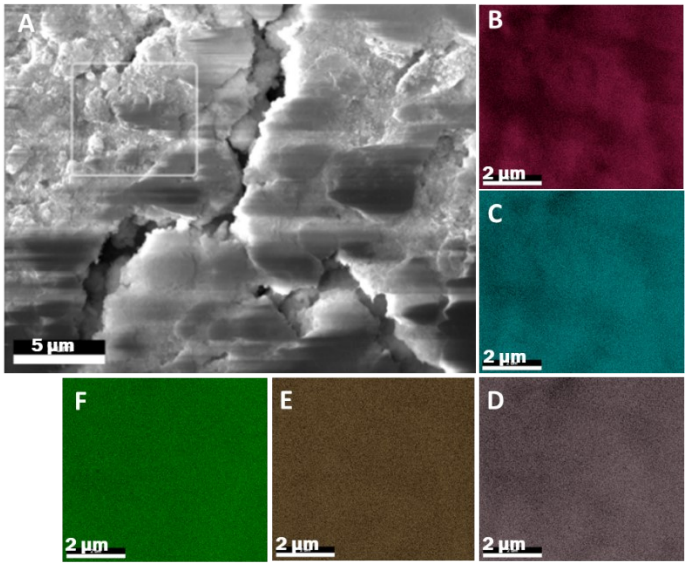


Fig S9 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOI in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 40^oC following UV-ozone



treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and I (F) atoms.

Fig S10 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for BiOI in an SiO_2 binder coated with 10 cycles of Al_2O_3 ALD at 40^oC without UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and I (F) atoms.

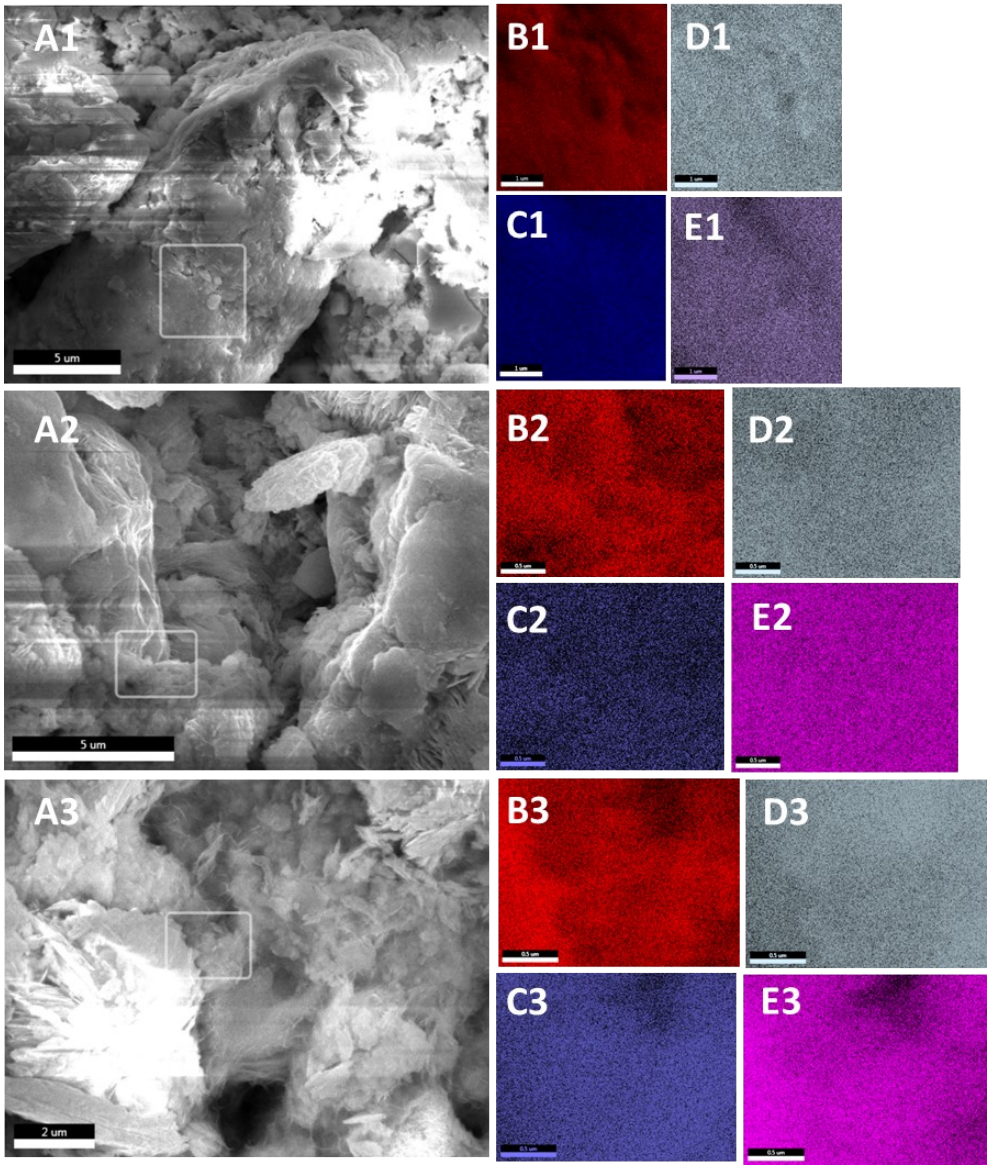


Fig S11 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for pure BiOCl-particle films with 10 cycles of Al_2O_3 ALD at (A1-E1) 40^{o}C, (A2-E2) 60^{o}C, (A3-E3) 80^{o}C, following UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Cl (F) atoms.

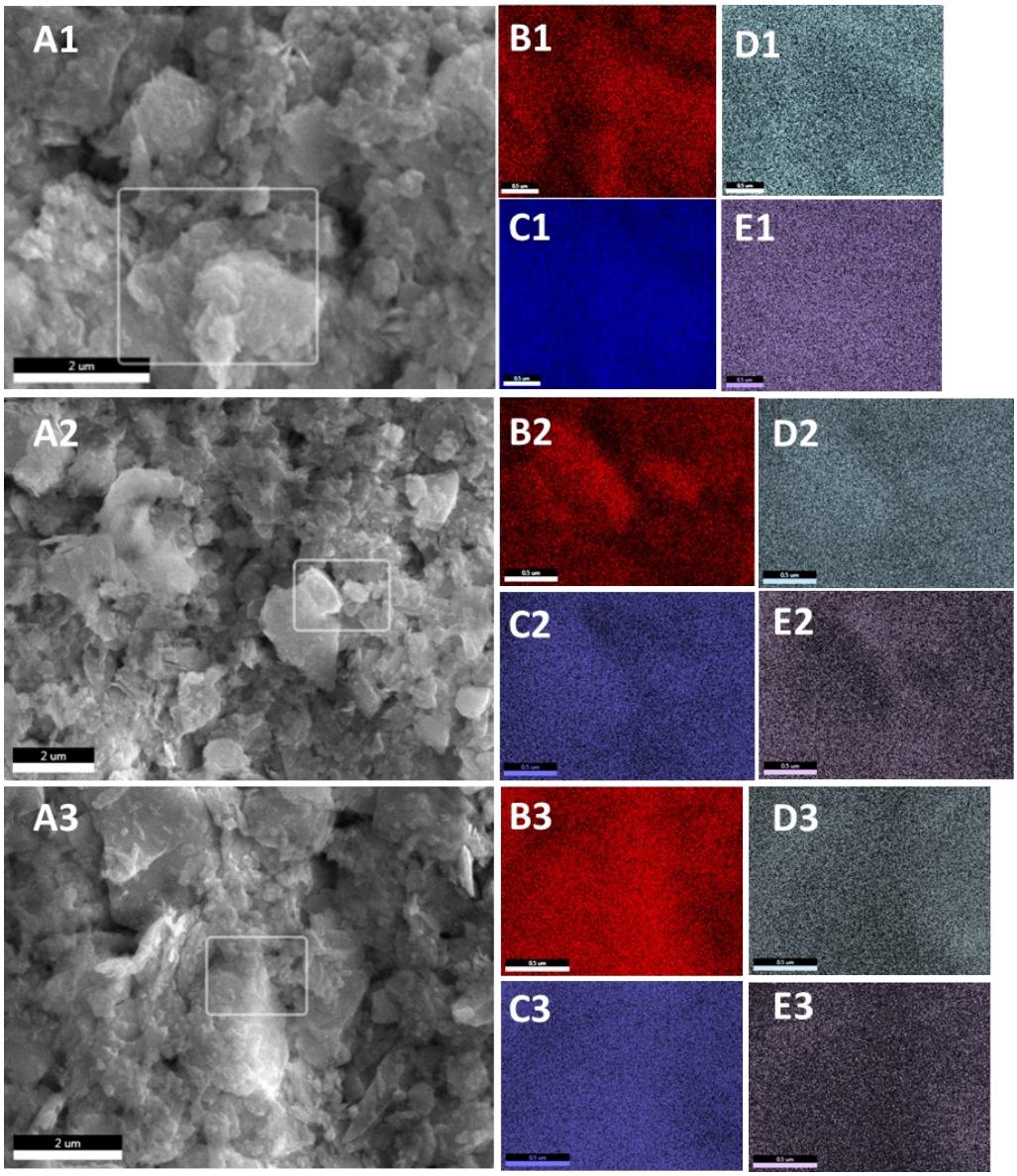


Fig S12 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for pure BiOBr-particle films with 10 cycles of Al_2O_3 ALD at (A1-E1) 40^{o}C, (A2-E2) 60^{o}C, (A3-E3) 80^{o}C, following UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and Br (F) atoms.

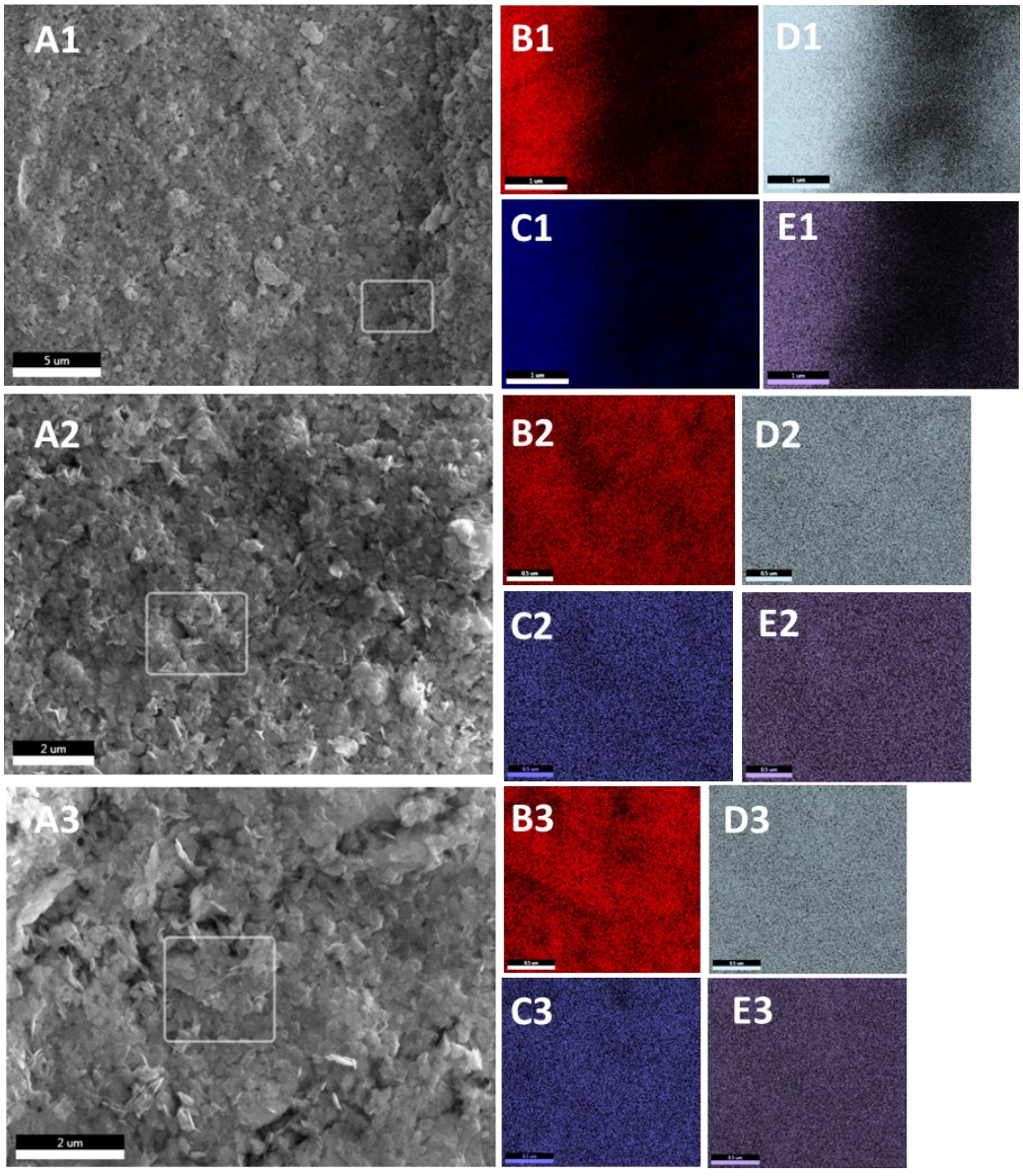


Fig S13 SEM micrograph (A) and EDS elemental maps (B-F) of the highlighted area for pure BiOI-particle films with 10 cycles of Al_2O_3 ALD at (A1-E1) 40^{o}C, (A2-E2) 60^{o}C, (A3-E3) 80^{o}C, following UV-ozone treatment. EDS legend: O (B), Al (C), Si (D), Bi (E) and I (F) atoms.

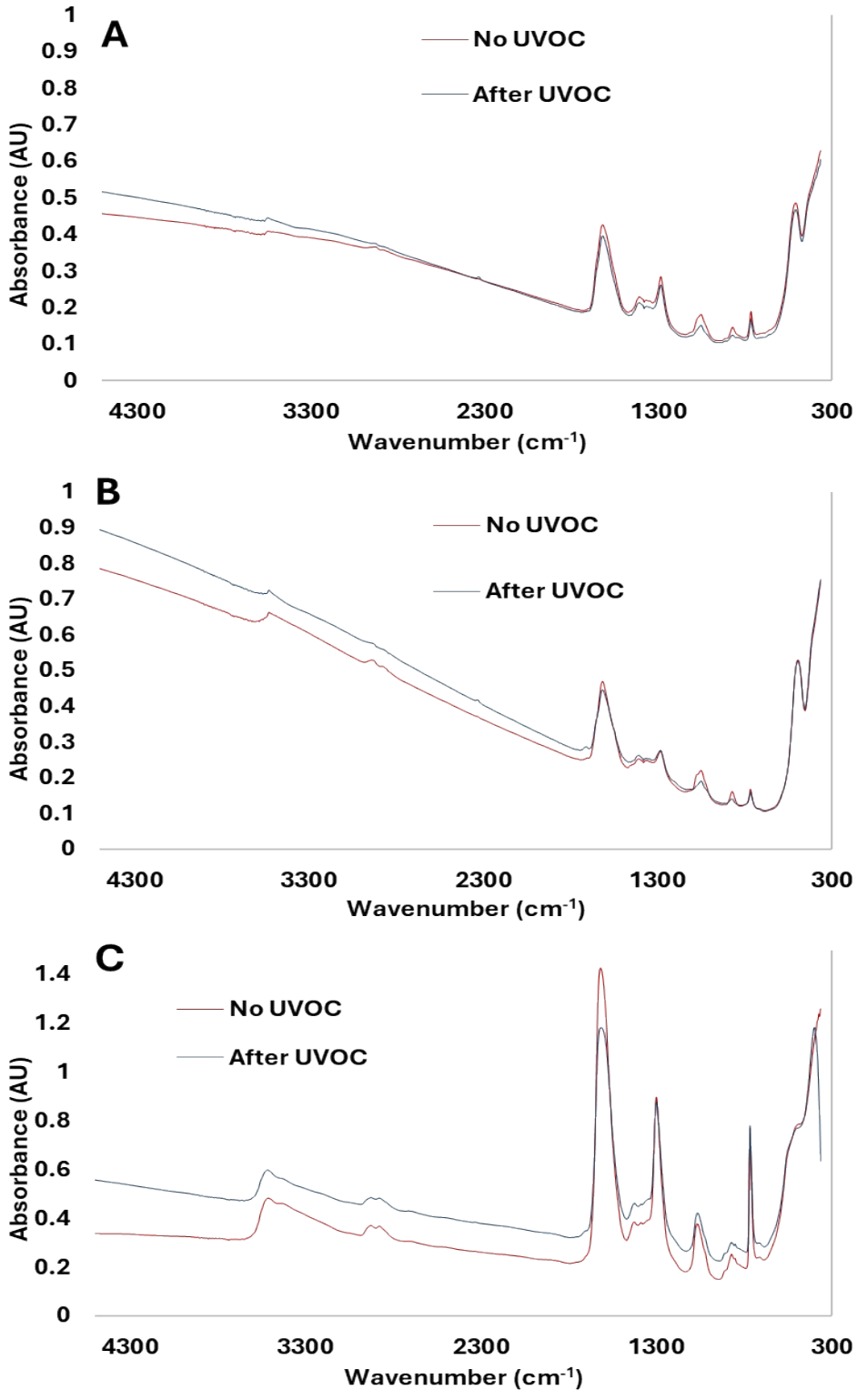


Fig S14 FTIR spectra measured for thin BiOX layers pressed on KBr pellets, with (blue) and without (red) UVOC treatment. Presented are traces for (A) BiOCl, (B) BiOBr and (C) BiOI.

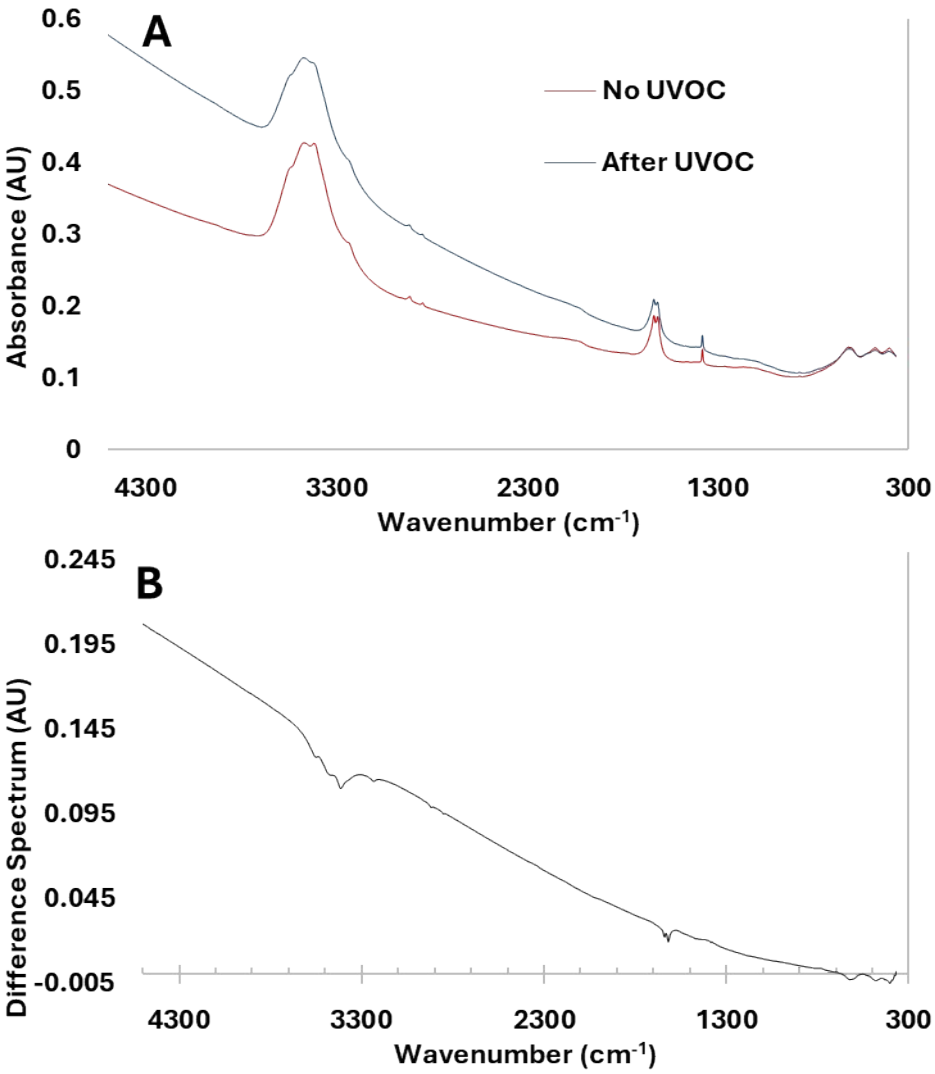


Fig S15 (A) FTIR spectra measured for KBr pellets, with (blue) and without (red) UVOC treatment, compared to a vacuum background. (B) Difference spectrum of the KBr before UVOC subtracted from the KBr following UVOC treatment.

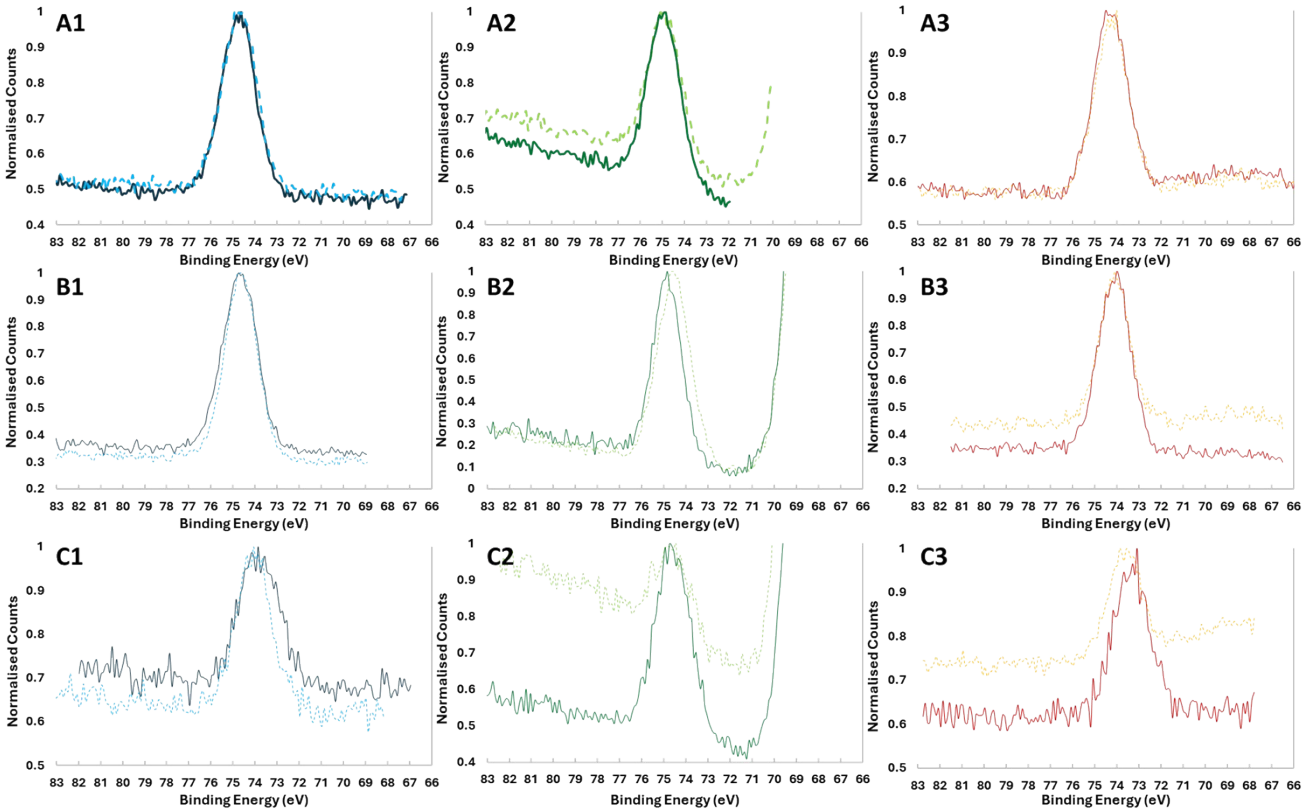


Fig S16 High resolution XPS Al2p peaks for samples with (continuous line) and without (dashed line) UV-ozone pre-treatment prior to coating with (A) 10 cycles, (B) 5 cycles, and (C) 1 cycle of Al_2O_3 on (1) BiOCl, (2) BiOBr, and (3) BiOI.

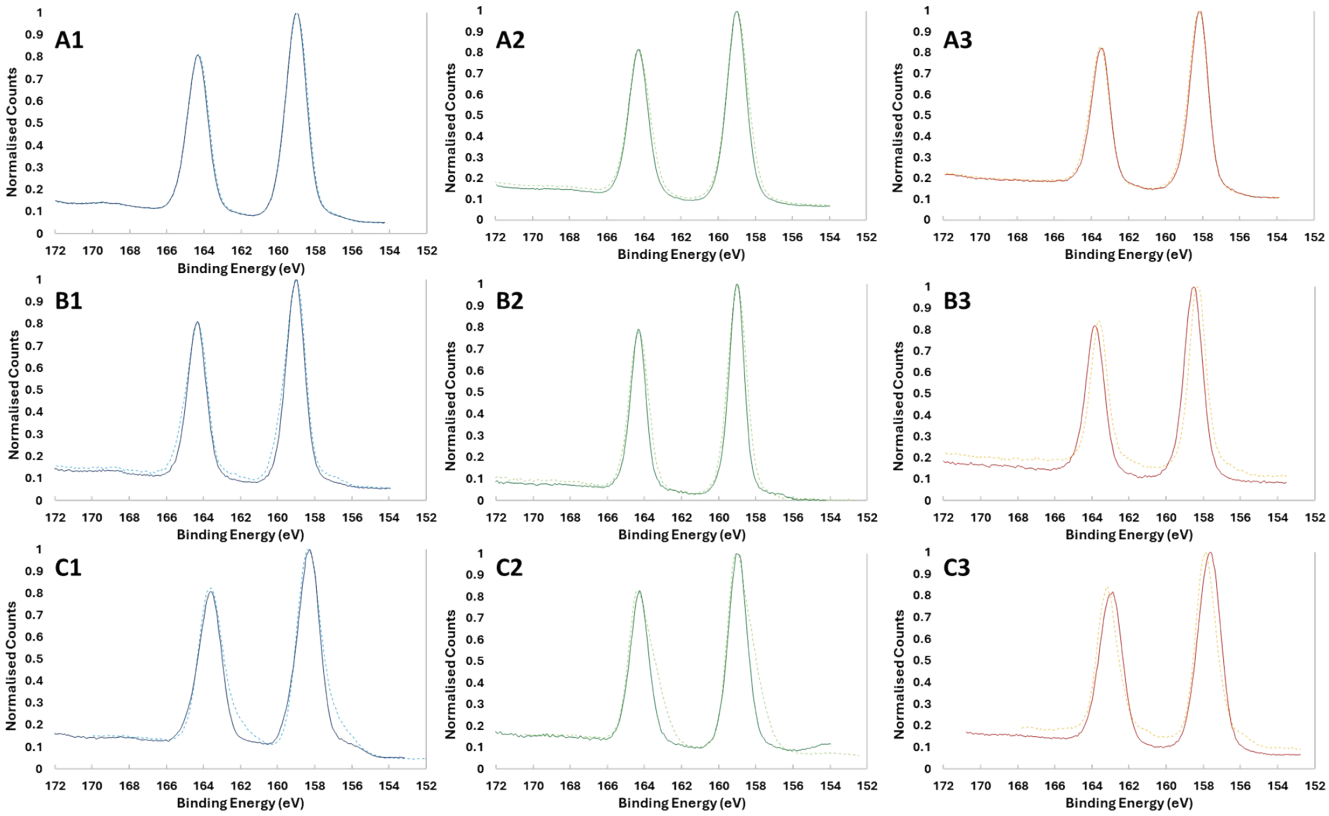


Fig S17 High resolution XPS Bi4f peaks for samples with (continuous line) and without (dashed line) UV-ozone pre-treatment prior to coating with (A) 10 cycles, (B) 5 cycles, and (C) 1 cycle of Al_2O_3 on (1) BiOCl, (2) BiOBr, and (3) BiOI.

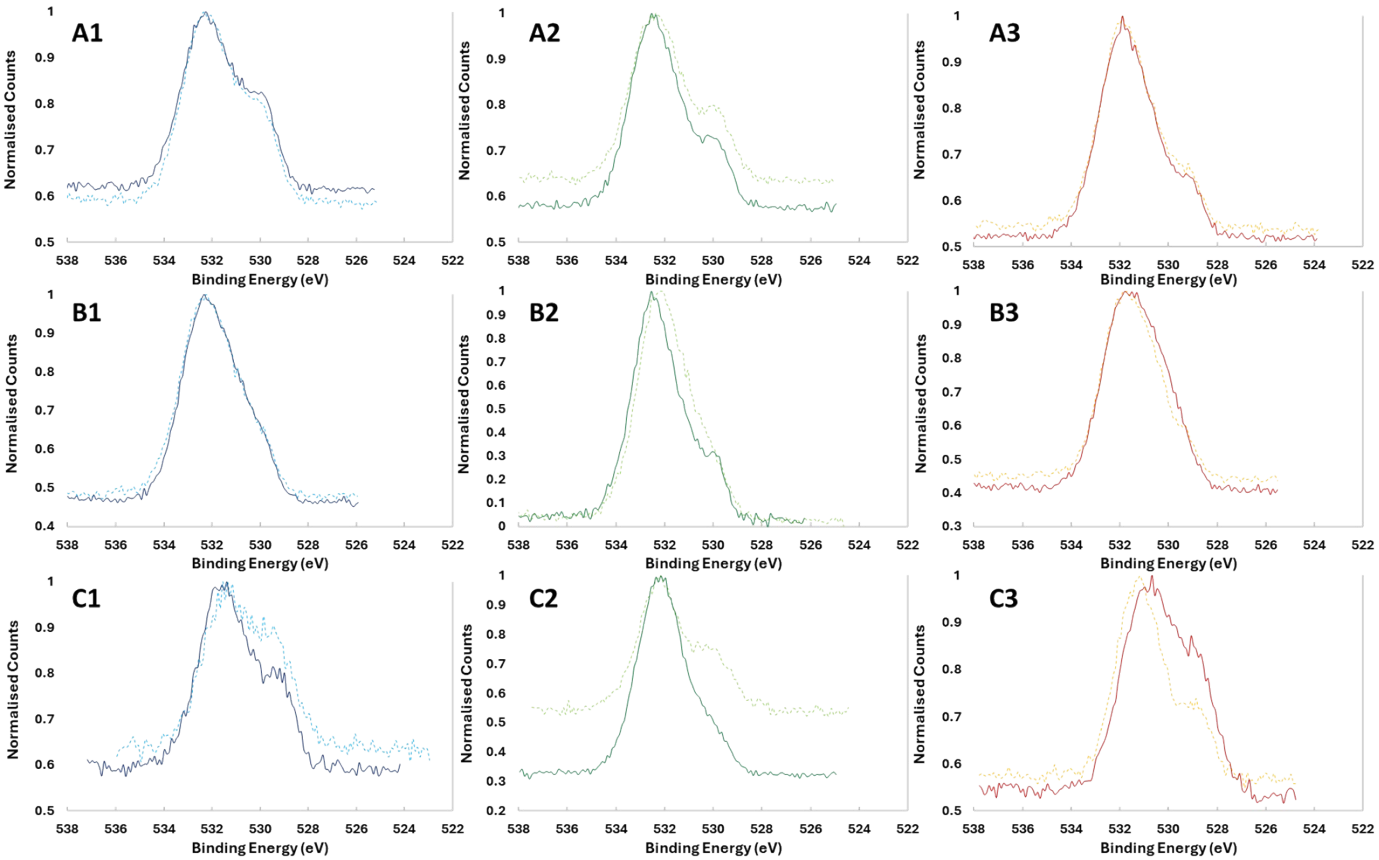


Fig S18 High resolution XPS O1s peaks for samples with (continuous line) and without (dashed line) UV-ozone pre-treatment prior to coating with (A) 10 cycles, (B) 5 cycles, and (C) 1 cycle of Al_2O_3 on (1) BiOCl, (2) BiOBr, and (3) BiOI.

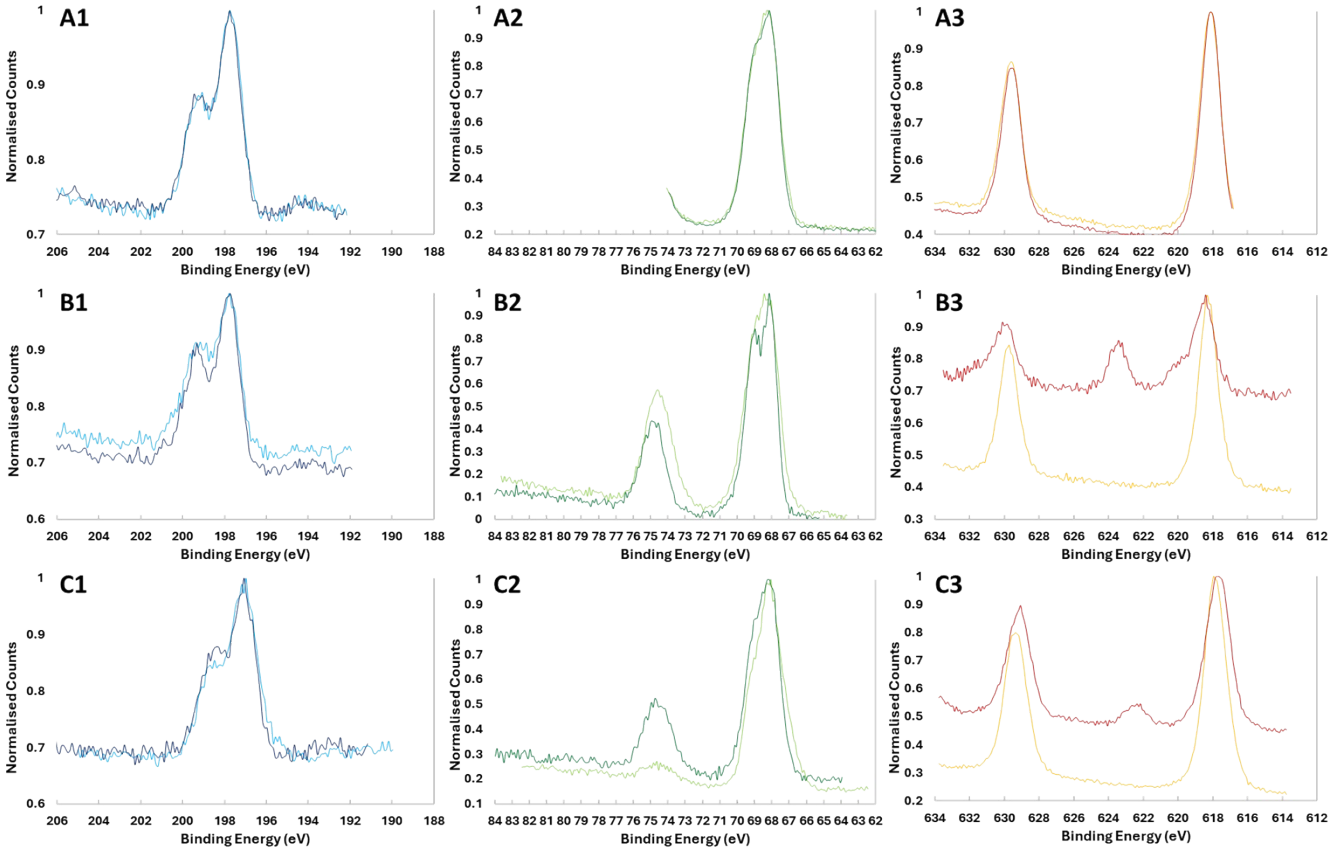


Fig S19 High resolution XPS Cl2p (1), Br2d (2) and I3d (3) peaks for samples with (continuous line) and without (dashed line) UV-ozone pre-treatment prior to coating with (A) 10 cycles, (B) 5 cycles, and (C) 1 cycle of Al_2O_3 on (1) BiOCl, (2) BiOBr, and (3) BiOI.

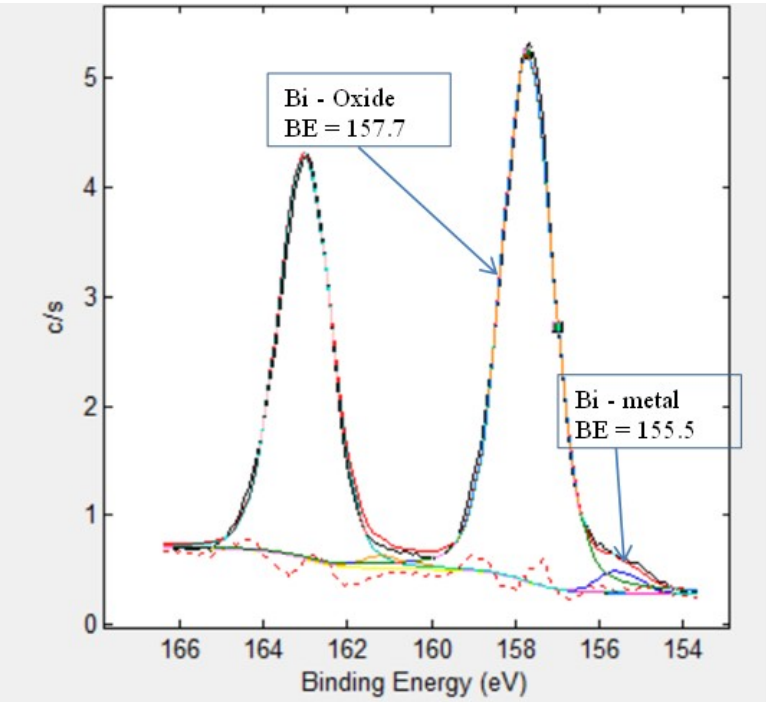
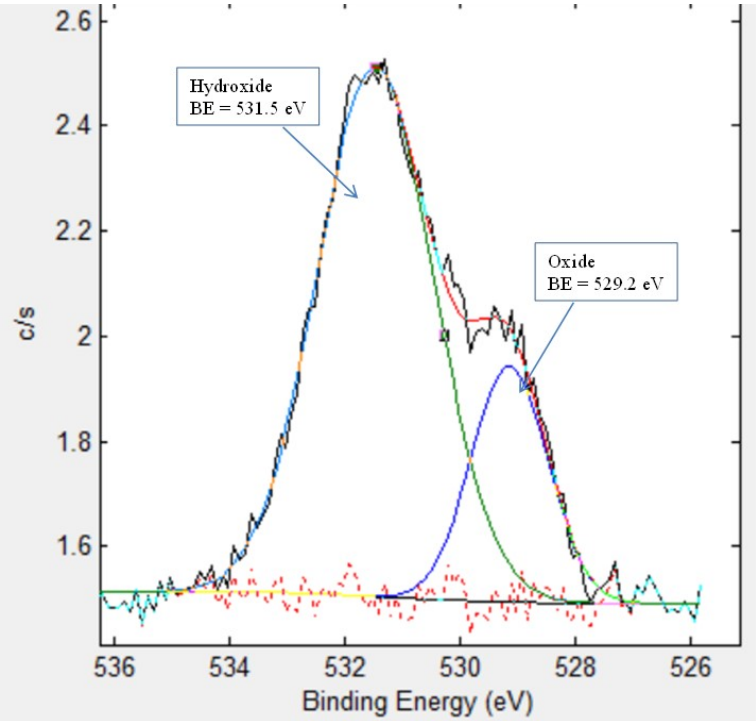


Fig S20 Bi4f line in a BiOCl sample coated with 1 cycle of ALD at 60°C, following UVOC pretreatment, deconvoluted into an asymmetric Bi-metal peak at 155.5 eV (FWHM = 1.3



eV) and a symmetric Bi-oxide peak at 157.7 eV (FWHM = 1.5 eV).

Fig S21 O1s line in a BiOCl sample coated with 1 cycle of ALD at 60°C, following UVOC pretreatment, deconvoluted into a symmetric oxide peak at 529.2 eV (FWHM = 1.6 eV) and a symmetric hydroxide peak at 531.5 eV (FWHM = 2.3 eV).

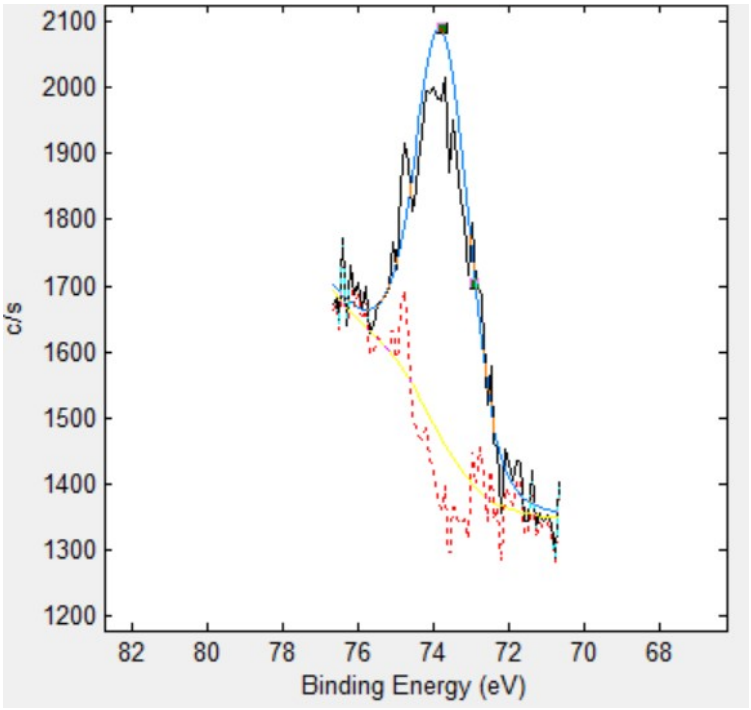


Fig S22 Al2p line in a BiOBr sample coated with 1 cycle of ALD at 60°C, following UVOC pretreatment, deconvoluted into a symmetric Al_2O_3 peak at 73.8 eV (FWHM = 1.7 eV).

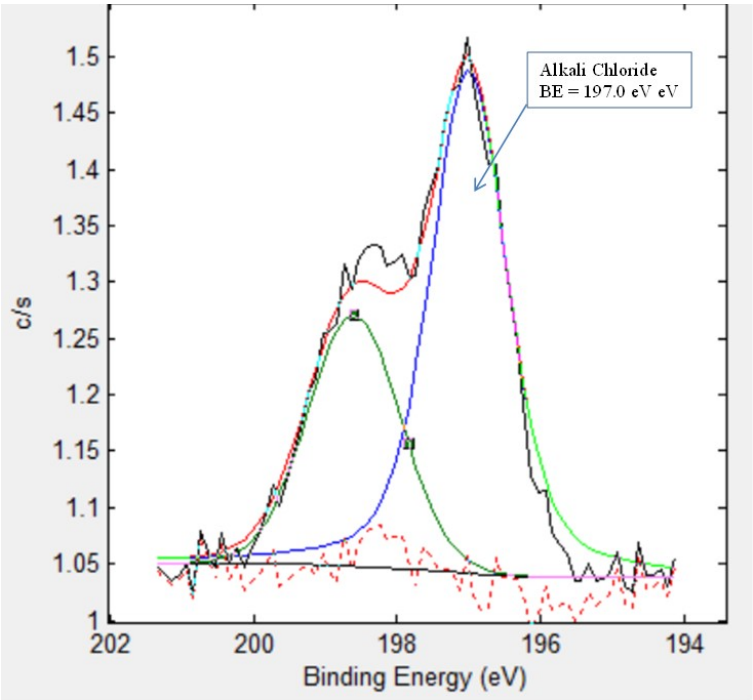


Fig S23 Cl2p line in a BiOCl sample coated with 1 cycle of ALD at 60°C, following UVOC pretreatment, showing two peaks with a spin-orbit splitting of 1.6 eV, with a symmetric peak at 197.0 eV (FWHM = 1.3 eV).

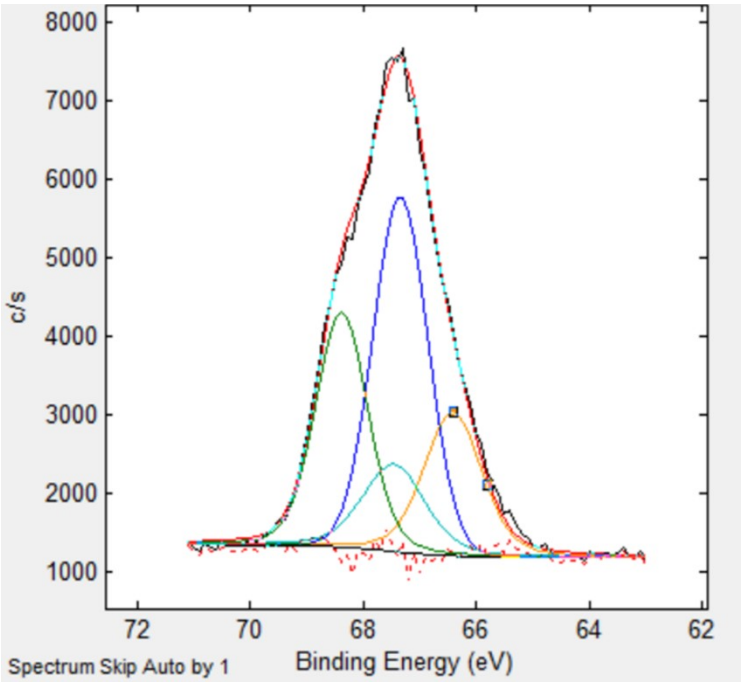


Fig S24 Br3d line in a BiOBr sample coated with 1 cycle of ALD at 60°C, following UVOC pretreatment, deconvoluted into two unallocated peaks with a spin-orbit splitting of 1.05 eV, a symmetric peak at 66.5 eV (FWHM = 1.4 eV) and a symmetric peak at 67.4 eV (FWHM = 1.1 eV).

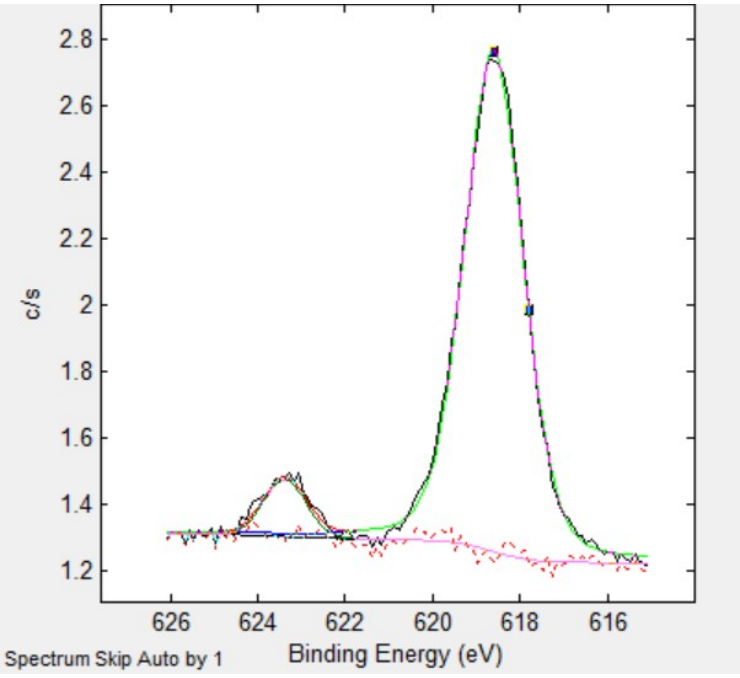


Fig S25 I3d5 line in a BiOI sample coated with 1 cycle of ALD at 60^{o}C, following UVOC pretreatment, deconvoluted into a symmetric alkali oxide peak at 618.7 eV (FWHM = 1.6 eV) and an asymmetric (IV) oxidation state peak at 623.4 eV (FWHM = 1.2 eV).

Table S1 T-test p-values for the comparison of kinetic data between samples coated with or without UVOC pretreatment. Data is shown for 5, 10, and 20 ALD cycle coatings deposited at 60°C, for each photocatalyst, as well as across all BiOX types.

Coating Thickness	**5 Cycles**	**10 Cycles**	**20 Cycles**
BiOCl	0.0174	0.000637	0.492
BiOBr	0.00966	0.211	0.25
BiOI	0.0207	0.0234	0.00909
All Catalysts	0.0151	0.0488	0.0639