ELECTRONIC SUPPLEMENTARY INFORMATION

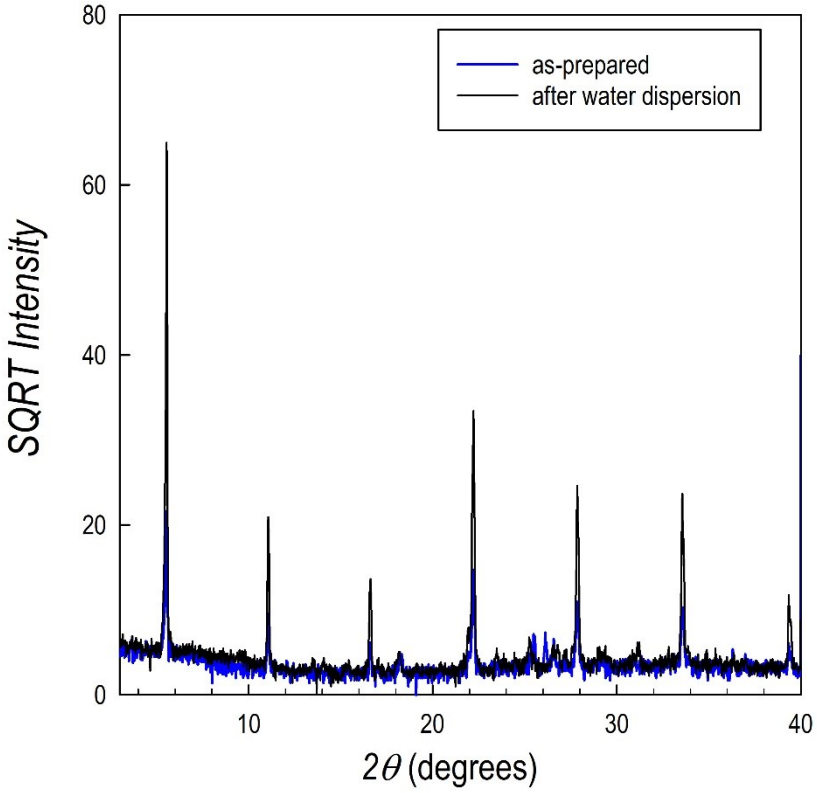

Figure S1. XRD (sqrt of intensity) patterns of PEA_2SnBr_4 synthesized by wet-chemistry (blue) and after recovery from DW (black)

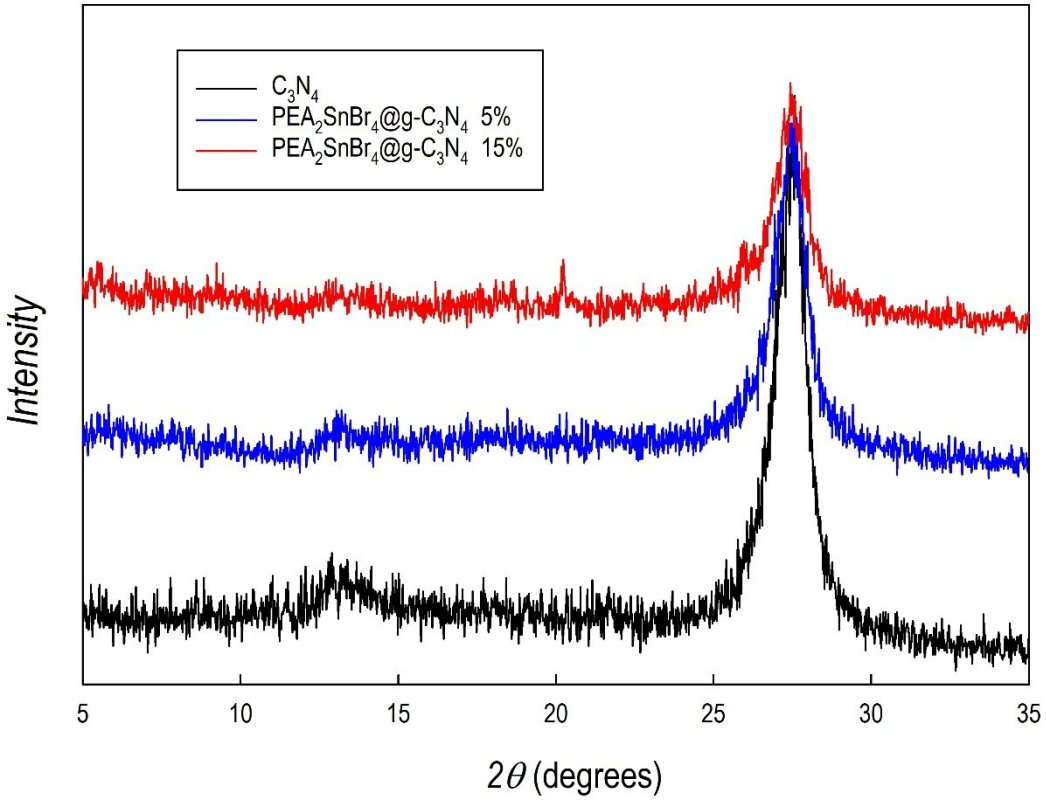

Figure S2 – XRD patterns of pure g-C_3N_4 and PEA_2SnBr_4@g-C_3N_4 composites at different percentages of perovskite loading.

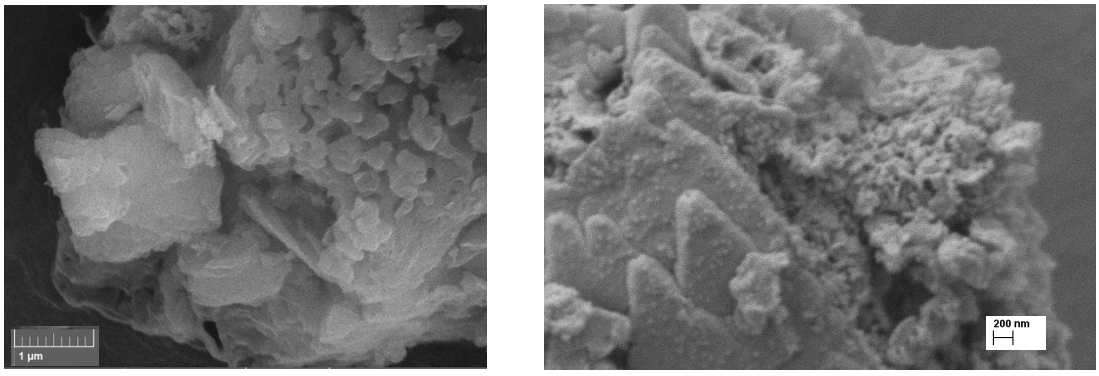

Figure S3. Representative SEM images collected on the pristine g-C_3N_4 (left) and on the PEA_2SnBr_4@g-C_3N_4 composites (15%, right).

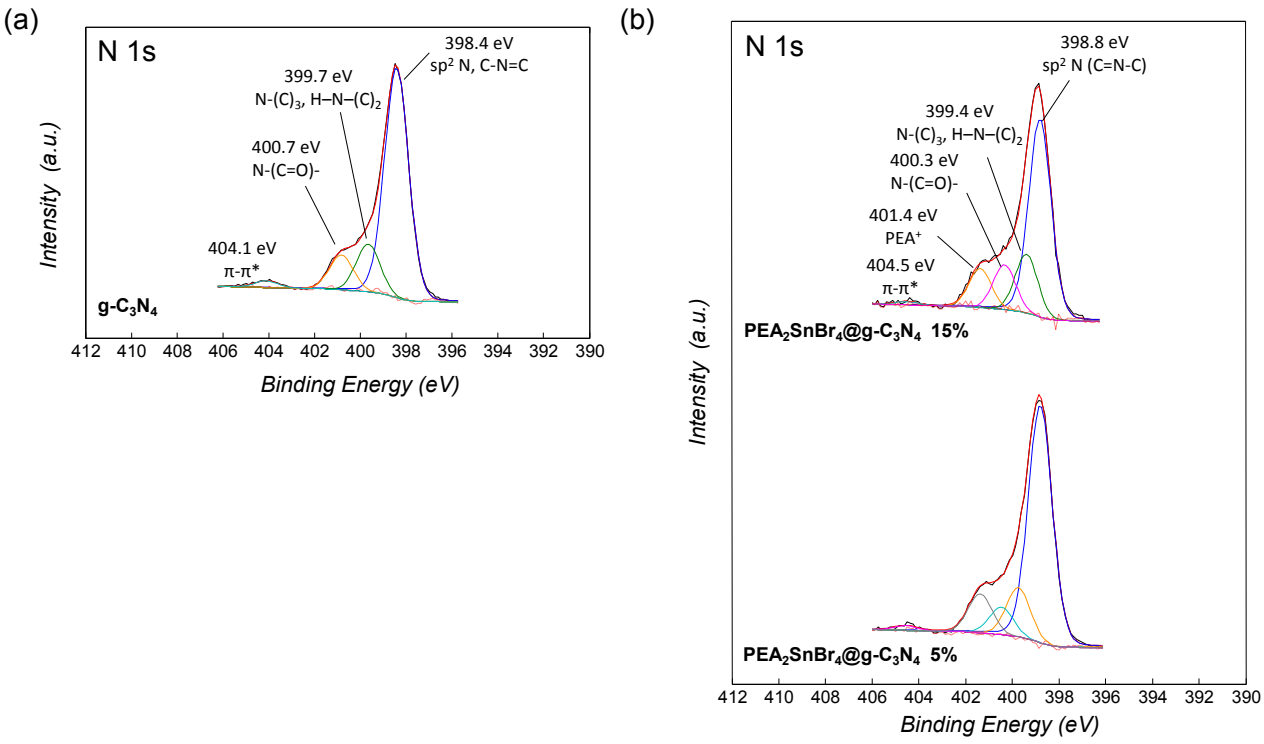

Figure S4: XPS N 1s spectra of the pristine g-C_3N_4 (a) and of the PEA_2SnBr_4@g-C_3N_4 composites (b).

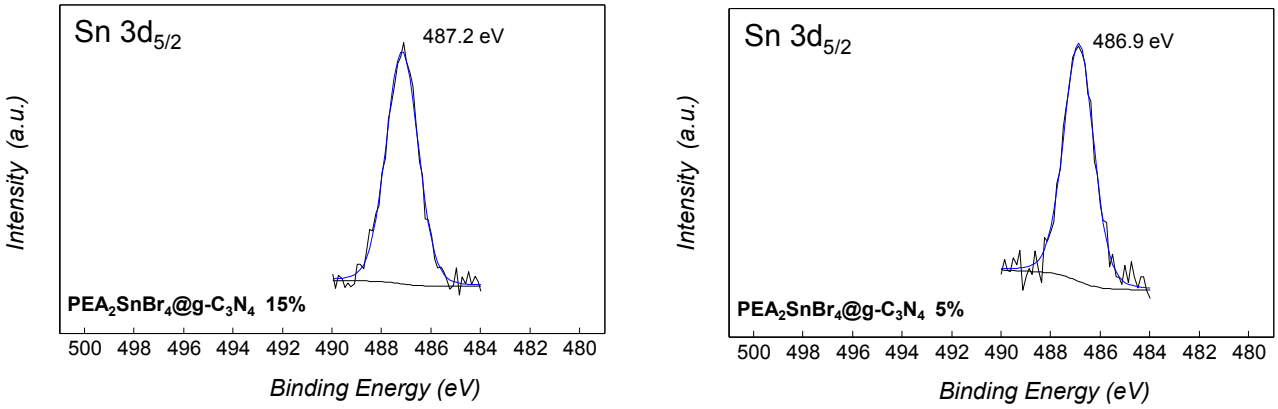

Figure S5: XPS Sn $3d_{5/2}$ spectra of the PEA_2SnBr_4@g-C_3N_4 composites.

Table S1 – Elemental composition of composite samples probed by EDX, e.s.d. for the measurements is around 5%.

Composite (perovskite %)	exp Br/Sn
5	3.79
5	4.04
5	3.91
15	4.02
15	4.01
15	3.96

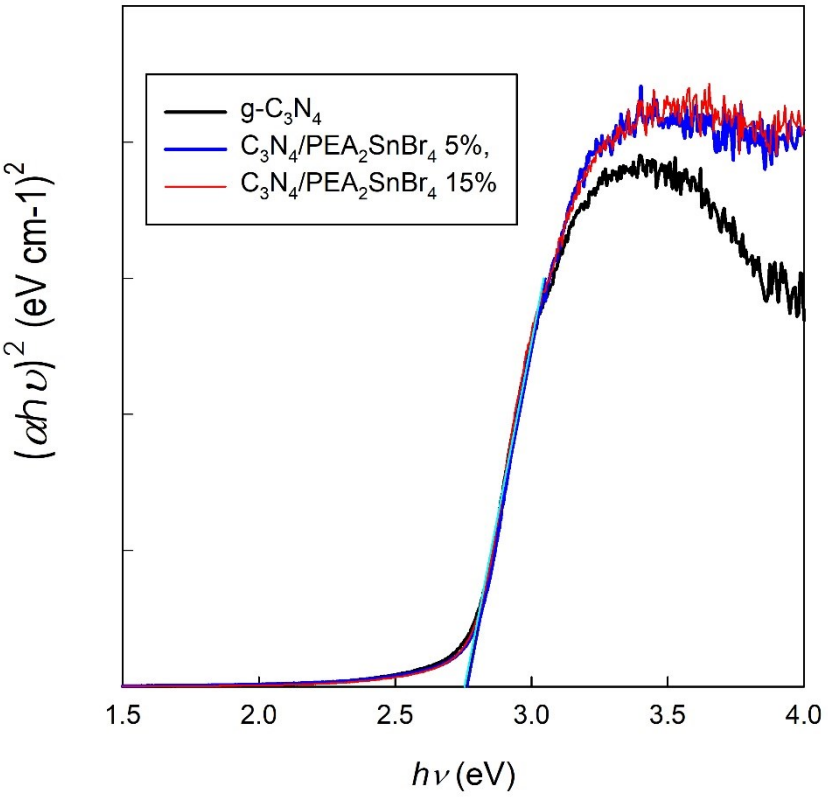

Figure S6 – Tauc's plots of pure g-C_3N_4 and PEA_2SnBr_4@g-C_3N_4 composites at different percentages of perovskite loading.

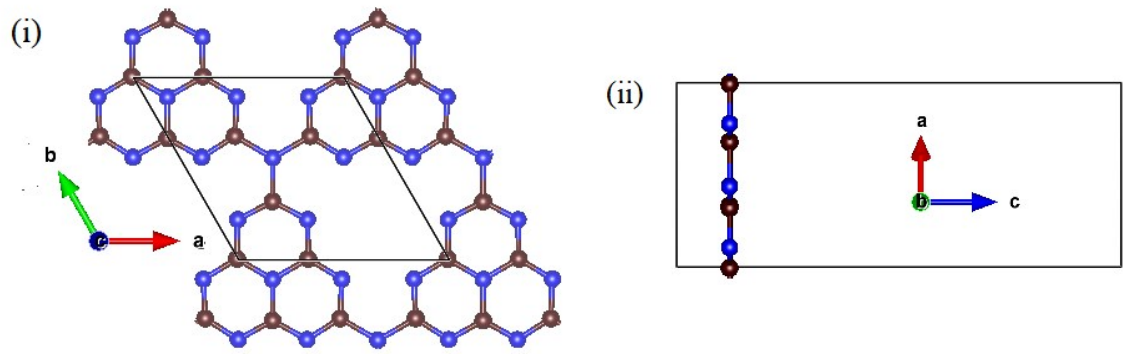

Figure S7: Optimized structure of g-C_3N_4 with highlighted unit-cell in (i) (110), and (ii) (101) planes. The black and blue balls represent C and N atoms, respectively. The unit cell is shown with (i) rhombus and (ii) rectangle.

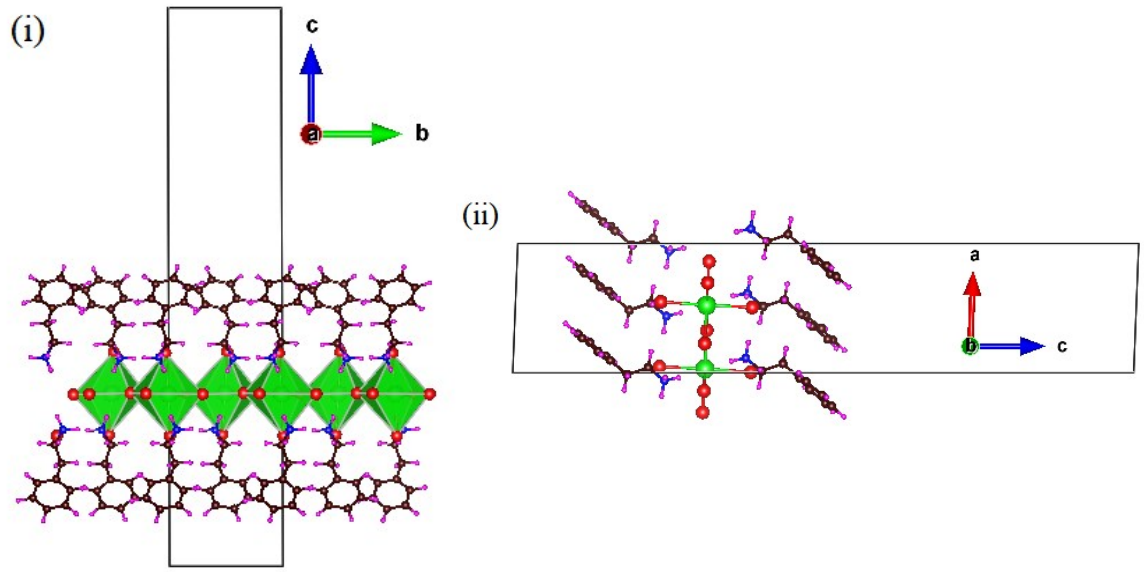

Figure S8: Optimized structure of PEA_2SnBr_4 monolayer in (i) (011) plane, and (ii) (101) plane. The rectangle represent the unit cell. The green, red, black, blue and magenta balls are representative of Sn, Br, C, N, and H atoms, respectively.

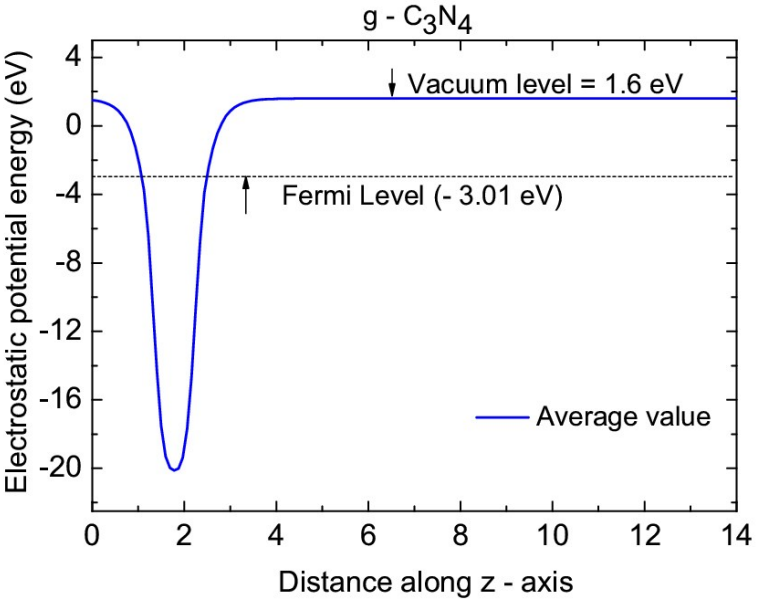

Figure S9: Electrostatic potential energy for g-C_3N_4 plotted along z-axis (Å) of unit cell.

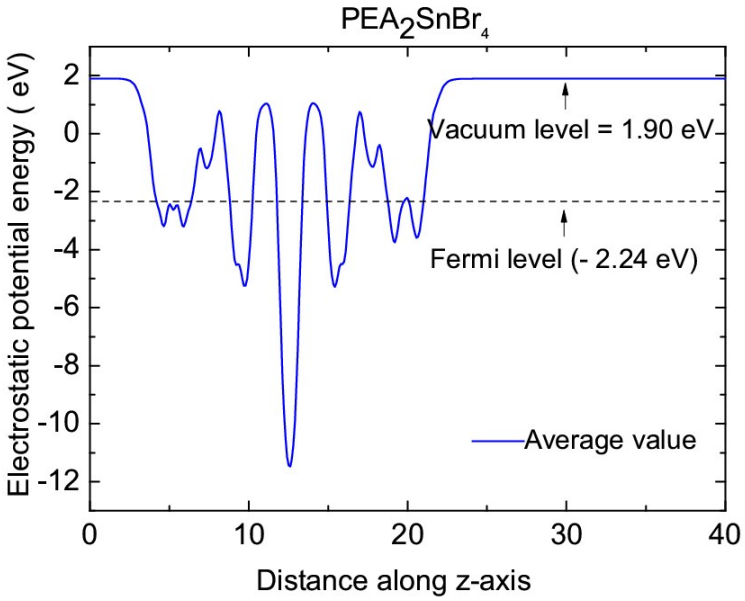

Figure S10: Electrostatic potential energy for PEA_2SnBr_4 monolayer along z-axis (Å).

Experimental Section

Synthesis and characterization of the catalysts

Bulk g-C_3N_4 has been synthesized from the polymerization of DCD ($NH_2C(=NH)NHCN$, Aldrich, 99%) by the following thermal treatment (under N_2 flux): heating (1°C/min) to 600 °C, isothermal step for 4 hours followed by cooling to room temperature (10°C/min). Synthesis has been carried out in a partially closed alumina crucible. PEA_2SnBr_4 has been prepared by dissolving PEABr and $SnBr_2$ in DMF and stirring, under nitrogen flux, the solution until dryness. The PEA_2SnBr_4@g-C_3N_4 composites have been prepared by adding to the DMF solution containing PEABr and $SnBr_2$ the proper amount of g-C_3N_4 prepared as described above.

The crystal structure of the samples has been characterized by room temperature Cu-radiation XRD acquired with a Bruker D8 diffractometer. DRS spectra were acquired in the wavelength range 300-800 nm directly on the powders by using a Jasco V-750 spectrophotometer, equipped with an integrating sphere (Jasco ISV-922). Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, TESCAN Mira 3) operated at 25 kV.

H_2 photogeneration and organic dye degradation in water

H_2 evolution experiments were conducted in distilled water containing 10% v/v triethanolamine (Aldrich, ≥ 99%) or 0.1 M glucose (99.9%, Carlo Erba Reagents), irradiated in Pyrex glass containers (28 mL capacity, 21 mL sample).[1] After addition of the catalyst (1 g L^{-1}), the sample was deoxygenated by Ar bubbling (20 min) to obtain anoxic conditions, and irradiated under magnetic stirring for 6 hours.

For the experiments involving use of Pt co-catalyst, Chloroplatinic acid (H_2PtCl_6, 38% Pt basis), used as Pt source, was from Sigma-Aldrich. Since Pt is *in situ* photodeposited on the catalyst surface, after Ar bubbling a small volume from a 15 g/L H_2PtCl_6 aqueous solution was added using a 10-100 μL micropipette to the catalyst suspension (1 g/L) in 10% v/v TEOA or 0.1 M glucose, directly in the photoreactor. The latter was closed with sleeve stopper septa and was irradiated, as described in the following, achieving simultaneous Pt deposition and H_2 production.[2] Irradiation was performed under simulated solar light using a Solar Box 1500e (CO.FO.ME.GRA S.r.l., Milan, Italy) set at a power factor 500 W m^{-2}, and equipped with UV outdoor filter made of IR-treated soda lime glass. Duplicate photoproduction experiments were performed on all samples. The headspace evolved gas was quantified by gas chromatography coupled with thermal conductivity detection (GC-TCD), as described in previous work.[1] The results obtained in terms of H_2 evolution rate are expressed in the

paper as μmoles of gas per gram of catalyst per hour (μmoles g^{-1} h^{-1}). XRD measurements on spent catalysts have been done by filtering the suspension and recovering the powder, which underwent diffraction measurements.

Methylene blue (MB) degradation tests were performed on 10^{-5} M MB aqueous solutions (150 mL, prepared in distilled water) in presence of 1 g/L of each catalyst, and with no catalyst to evaluate direct photolysis. Before irradiation, magnetic stirring for 30 min in the dark was performed to allow MB adsorption equilibrium on the catalyst. Irradiation was done under simulated solar light (250 W/m^2): at specific time intervals, 1.5 mL of sample was withdrawn, centrifuged at 3000 rpm for 5 min and the absorbance (664 nm) of the supernatant solution was recorded by an UVmini-1240 UV–vis spectrophotometer (Shimadzu Corporation).

Metal leaching tests

The leaching tests were performed by dispersion of the as-prepared PEA_2SnBr_4 powder in distilled water, under magnetic stirring for 4 h. Then the suspension was filtered on 0.2 μm nylon membrane and the amount of tin in solution was determined by ICP-OES analysis, after acidification (1% v/v ultrapure nitric acid).

XPS Measurements

XPS analyses were carried out with a Scanning XPS Microprobe (PHI 5000 Versa Probe II, Physical Electronics) equipped with a monochromatic Al K_α X-ray source (1486.6 eV), operated at 15 kV and 24.8 W, with a spot size of 100 μm. Survey (0–1200 eV) and high resolution spectra (C 1s, O 1s, N 1s, Br 3d and Sn 3d) were recorded in FAT (Fixed Analyser Transmission) mode at a pass energy of 117.40 and 29.35 eV, respectively. Surface charging was compensated using a dual beam charge neutralization system, with a flux of low energy electrons (~1 eV) combined with very low energy positive Ar^+ ions (10 eV). The hydrocarbon component of C1s spectrum was used as internal standard for charging correction and it was fixed at 284.8 eV. All spectra were collected at an angle of 45° with respect to the sample surface. Best-fitting of the high resolution spectra was carried out with MultiPak data processing software (Physical Electronics).

Computational Details

The calculations are performed using plane wave projector augmented wave (PAW)[3] pseudopotential method as implemented in Vienna *Ab initio* Simulation Package (VASP).[4] The exchange-correlation functional is treated within generalized gradient approximation (GGA) of Perdew, Burke, and

Ernzerhof (PBE)[5] for structural optimization using 5x5x1 ***k***-points mesh. The unit cell dimensions (shape and cell volume) as well as the ionic positions are relaxed until the absolute value of force on each ion becomes less than 0.005 eV/Å. The vacuum spacing between the layers are taken to be 20 Å to eliminate the inter-layer interactions. The optimized structure of g-C_3N_4 and PEA_2SnBr_4 monolayers are shown in Figures S4 and S5, respectively. After that, the electrostatic potential energy and band gap values are calculated with Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional.[6] The value of work function is calculated by taking the difference between the Fermi level and the electrostatic potential energy in vacuum (Figures S6 and S7).

References

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