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$CsPbBr_3$ nanocrystals supported on partially oxidized Ti_2N MXenes for photothermal CO_2 conversion

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Abstract:

The development of new photo-thermal catalysts for the transformation of CO_2 into fuels is of great interest, offering a clean and sustainable approach to reducing the carbon footprint. Herein, we present a novel hybrid material composed of nanocrystalline metal halide perovskite ($CsPbBr_3$) supported on two-dimensional titanium nitride (Ti_2N) MXene. Additionally, we demonstrate the importance of forming an external TiO_2 layer through partial oxidation of the MXene (POM-Ti_2N), which introduces catalytic centers and enhances photogenerated charge separation. Remarkable activity in the formation of CH_4 and CO was observed, with yields of 321 $\mu mol \cdot g^{-1}$ and 480 $\mu mol \cdot g^{-1}$, respectively. The selectivity of the reaction was found to be temperature dependent. The mechanism was thoroughly investigated using XPS and photoluminescence studies. XPS analysis revealed a significant chemical interaction between the $CsPbBr_3$ nanocrystals and the POM-Ti_2N MXene after the formation of the composite. Photoluminescence measurements revealed a considerably shorter emission lifetime for the hybrid catalyst (τ_{ave} = 1.73 ns) compared to that of the $CsPbBr_3$ nanoparticles (τ_{ave} = 25.32 ns), indicating strong interaction with the MXene. Furthermore, this research highlights the potential of combining metal halide perovskites with MXenes and the importance of controlling their interface for photo-thermal reactions.

1. Introduction

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Researchers are making significant efforts to address climate change by developing CO_2 utilization technologies that convert this molecule into chemicals. Solar-driven photothermal catalysis is a compelling and sustainable approach that harnesses light and heat energy to synergetically convert CO_2 into fuels and valuable chemicals.[1,2] There are many photothermal catalytic pathways that offer sustainable routes for CO_2 valorization,[3,4] such as the Sabatier reaction, which has been one of the most studied reactions for over a century since its discovery. This reaction consists of the hydrogenation of CO_2 to CH_4, which is thermodynamically favorable but is hindered by slow reaction kinetics, therefore, the use of high temperatures is necessary to activate the CO_2 molecule. The photothermal catalytic mechanism includes multiple proton-coupled electron transfer to CO_2 to form CH_4, which requires control of intermediate species on catalytic surfaces, often resulting in reduced selectivity and lower overall activity.[5]

In the classical thermal methanation process, the most studied metallic active centers are Ni, Ru, and Rh, which require high temperatures (300 to 400 °C) and pressures (5-20 bar) to achieve high efficiencies. However, the photothermal pathway can promote the Sabatier reaction under milder conditions, employing the same active sites supported on a semiconductor, with metal oxides being the most commonly used due to their robustness under reaction conditions. Recent studies showed that nickel (Ni) has emerged as the optimal compromise, delivering Ru-like activity when properly nanostructured on TiO_2 or CeO_2 supports.[6–8] Other researchers used single atoms and nanoparticles of ruthenium supported on $CeAlO_x$, achieving formidable catalytic performances.[9] Although a huge number of materials have been already explored to boost the photocatalytic side of the photothermal reaction (e.g. metal oxide, MOFs, COFs, metal complex, C_3N_4…)[10–13] there is still a need to boost this reaction at lower temperatures (< 250 °C).

Metal halide perovskite nanocrystals (NCs) semiconductors have been extensively studied because they offer a wide range of applications due to their excellent optoelectronic properties, such as broad absorption in the UV-Vis spectrum, tuneable light absorption range, long charge diffusion length, and high molar extinction coefficients.[14] All these properties make them potential candidates for multiple photocatalytic applications. However, to improve the photocatalytic activity of pristine $CsPbBr_3$, it has been combined with other materials, on the one hand, to improve charge separation properties through charge migration and, on the other hand, to add better active catalytic sites.[15,16] In this regard, MXenes materials as a new type of two-dimensional (2D) structure, have recently attracted great attention due to their interesting

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properties such as rich surface chemistry, modifiable electronic structure and thermal stability. MXenes are transition metal carbides or nitrides with the general formula $M_{n+1}X_nT_x$ (n=1, 2 or 3), where M corresponds to a transition metal, X can be C or N, and T_x indicates the surface functional groups (usually -F, -O or -OH). These functional groups play an important role in the adsorption/desorption of molecules and electron transfer properties. Currently, in photothermal reduction of CO_2, there are a few examples in the literature studying the catalytic properties of MXene carbides containing perovskite NCs. For instance, aerogels of $CsPbBr_3/Ti_3C_2Tx$ MXene showed that Ti_3C_2Tx MXene's conductive network promotes charge separation from photoexcited $CsPbBr_3$, while its surface terminations (-O, -F, -OH) improve CO_2 adsorption, outperforming individual components.[17]

In addition, partially oxidized 2D transition metal carbides MXenes, also offer the possibility to decorate the titanium nitride MXene with TiO_2 moieties. According to the work of Pazniak et al.[18], the enhanced charge carrier exchange at the TiO_2/MXene interface enhances the sensing properties due to the formation of a depletion region between the metal and the semiconductor interface.[19]

The novelty of this work rely in the use for the first time of titanium nitride (Ti_2N) MXene in the Sabatier reaction. Therefore, within this context, we have beem the first investigating the formation of a novel hybrid material composed of nanocrystalline $CsPbBr_3$ supported on two-dimensional titanium nitride (Ti_2N) MXene for photo-thermal CO_2 conversion. To date, there is no report describing this specific combination. Although bare metal nitride MXenes can exhibit certain limitations in this reaction, we addressed this by forming external TiO_2 moieties through partial oxidation of the Ti_2N MXene and combining it with the perovskite nanocrystals. We evaluated the catalytic activity under different conditions and assessed its reusability, concluding that this hybrid is capable of performing CO_2 revalorization. XPS analysis and photophysical studies were carried out. Finally, we propose a working mechanism based on the formation of a heterojunction architecture, featuring an interlayer that inhibits direct charge recombination.

2. Results and discussion

$CsPbBr_3$ perovskite NCs and the Ti_2N MXenes were prepared separately according to the synthetic procedure described in detail in the Materials and Methods (see Supporting Information) and illustrated in Scheme 1 The synthesis of $CsPbBr_3$ NCs was carried out by the hot injection method[20]. Scheme 1a) shows the conventional preparation of the NCs through

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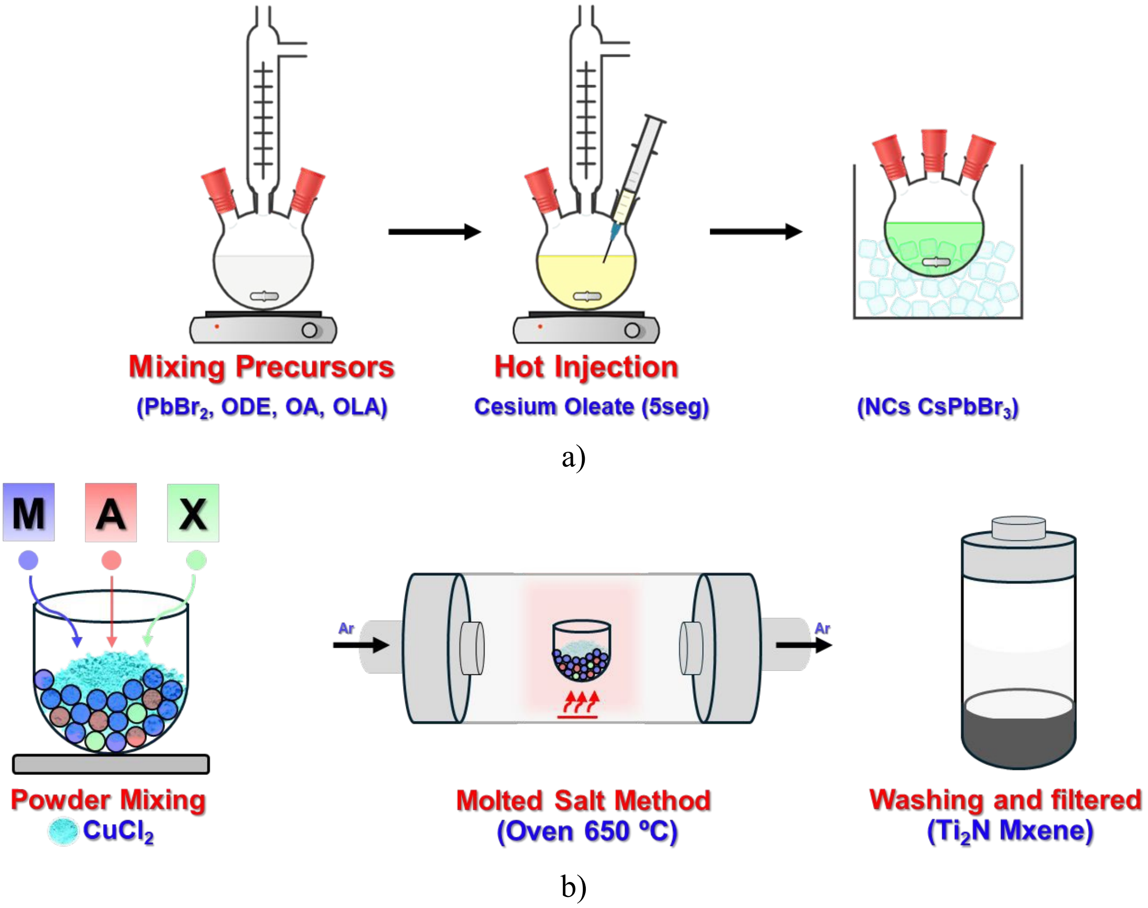
three sequential steps: i) mixing the precursors in a three-neck flask at elevated temperature, ii) rapid injection of the cesium precursor, and iii) immediate quenching in an ice-cold water bath. Regarding the preparation of partially oxidized multilayer Ti_2N MXene (POM-Ti_2N) involves two main stages: i) first the MAX phase was treated with $CuCl_2$ using the molten salt method at high temperature (650 ºC), followed by copper removal using persulfate solution, and ii) afterwards the solid was filtered and thoroughly washed with deionized water. It is during the purification with persulfates salts at 70 ºC, when a thin layer of small nanoparticles of TiO_2 were grown on top of the surface resulting in the partial oxidation of the T_2N MXene. (see Scheme 1b). Actually, TiO_2 presence is residual if the purification is carried out during same time and at room temperatures.

Finally, the perovskite NCs were supported onto POM-Ti_2N by after dispersing the POM-Ti_2N with ultrasonication in hexane and added dropwise a concentrated suspension of NCs. After a time, the solid was recovered by filtration. More details are described in the Materials and Methods (Scheme 1c).



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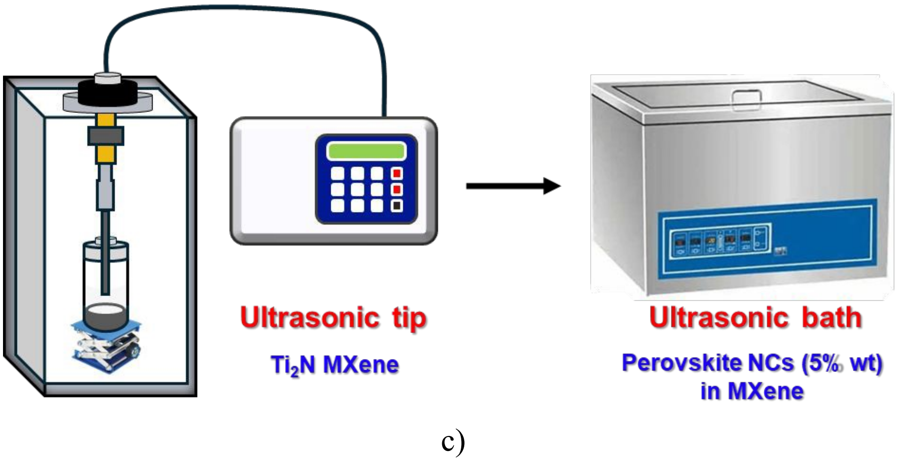

Scheme 1. Synthetic procedure for the preparation of the catalyst. a) Preparation of the $CsPbBr_3$ NCs, b) Formation of the Ti_2N MXene from the MAX phase and c) impregnation process for the deposition of the $CsPbBr_3$ NCs on the exfoliated Ti_2N MXene.

The synthesis of M-Ti_2N was carried out according to publication by Xinbo Liu et al., following the molten salt method, in which molar ratios between 1:3 and 1:4 with respect to Ti_2NAl:$CuCl_2$ are used. In our case, ratios of 1:4 were chosen to synthesise the multi-layered T_2N MXene.[21] In fact, analysis carried out with X-ray diffraction spectroscopy shown in Figure S4, confirms that the titanium nitride MXene synthesized by the molten salt method leads to a nitride with the crystal structure of α-TiN with characteristic peaks at 37.9º, 43.3º and 62.7º according, respectively, to the planes (004), (103), and (110).[22,23]

A slight modification of the purification procedure during the bath with persulphate salts, such as raising the temperature of the process or increasing the concentration of this salt, leads to a modification of the chemistry of the surface of the MXene layers by superficially oxidising the M-Ti_2N layers as can also be seen in Figure S4 with the appearance of new TiO_2-related signals, at $2\theta = 25.3º, 47.9º, 54.4º$ and $2\theta = 27.4º, 43.3º$ assigned to (101), (202), (211) anatase and (110), (111) rutile crystalline planes.

Furthermore, XRD analyses were performed for all the materials. The XRD results were trustworthy with the ICSD data file, #204325[24] which confirms the cubical crystalline structure of the $CsPbBr_3$ NCs, evidenced by the presence of the peaks at the angles 15º and 30º, which represent the (001) and (002) crystalline planes of the cubic perovskite crystals (Figure 1b). Once the NCs@POM-Ti_2N composite has been formed, it is not possible to visualise the signals due to the NCs due to their low concentration in the sample (<5% by weight) and the small amount of material used during the analysis (Figure 1a).

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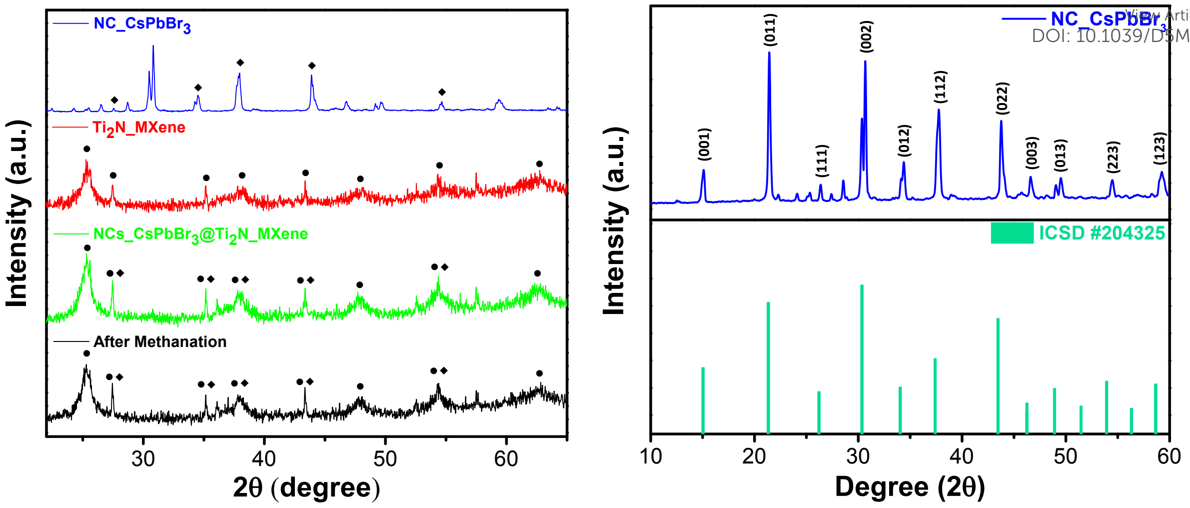

a) b)

Figure 1. a) Comparative XRD pattern of $CsPbBr_3$ NCs (blue), POM-Ti_2N MXene (red), NCs@POM-Ti_2N before (green) and after the catalytic reaction (black), b) $CsPbBr_3$ NCs compared with reference data from the ICSD #204325 data file.

Moreover, high-resolution transmission electron microscopy (HR-TEM) was used to study the $CsPbBr_3$ NCs and the Ti_2N MXene independently. Figure 2a shows that the perovskites NCs particles have a similar size and crystallinity. The particle size distribution of NCs was estimated using HR-TEM, yielding an average size of 5 nm (Figure 2b).

High resolution field emission scanning electron microscopy (HR-FESEM) is a useful tool to distinguish between the formation of multi-layered Ti_2N MXene (M-Ti_2N) and POM-Ti_2N. A soft purification treatment with 0.1M of sodium persulfate at room temperature leads easily to purification of M-Ti_2N with a minor structural defect, as shown in Figure 2c; whereas the same concentration of persulfate, but treating the MXene at 70 ^{o}C, produced a slight oxidation of the MXene surface, forming the POM-Ti_2N (see Figure 2d). Also, HR-FESEM images in Figure S5 reveal the formation of rugosity on the surface and edges of the Ti_2N MXene layers with the appearance of little crystals of TiO_2 homogenously dispersed. Additionally, interplanar distances measured with HR-TEM on layers of the POM-T_2N sample confirm the simultaneous presence of Ti_2N and TiO_2 crystals. (Figure 2e) After the formation of the composite NCs@POM-Ti_2N no evident changes are seen by HR-FESEM in the partially oxidated MXene particle; (Figure 2f) however, the dispersion of NCs particles on the POM-Ti_2N MXene is confirmed with DF STEM images in Figure S6. This image showed that elements that form the perovskite particles are well dispersed and distributed homogenously over the support. A clearer image that shows the physical presence of perovskites NCs on the POM-Ti_2N support is shown in Figure S7, from which we can estimate a loading of 5% per weight of NCs on the POM-Ti_2N MXene.

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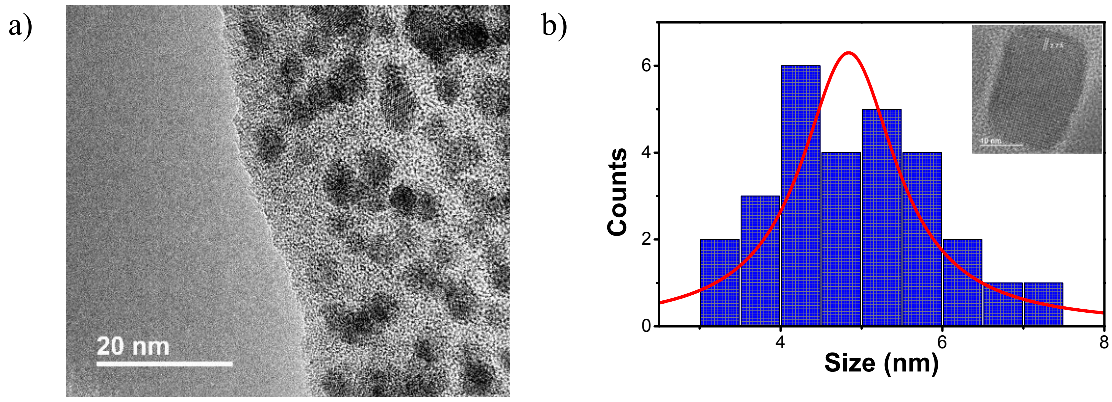
To elucidate the fine structure of the hybrid, HR-TEM images of NCs@POM-Ti_2N are presented in Figure 2g-h. As shown in Figure 2g, TiO_2 nanoparticles are uniformly anchored onto the Ti_2N MXene sheets, forming a surface-decorated[25] hybrid. This observation confirms that the partial surface transformation of Ti_2N into TiO_2 occurs during processing, yielding a coherent TiO_2/Ti_2N heterostructure.[26]

The distinct lattice fringes observed for both phases further verify the successful formation of the composite (Figure 2h). Spacings of 3.50 Å and 2.70 Å, as well as 2.10 Å, correspond to the (101) planes of anatase TiO_2[26] and the $(01\bar{1}0)$ planes of Ti_2N,[27,28] respectively. In addition, the lattice fringes of 3.00 Å are assigned to the (200) planes of $CsPbBr_3$ nanocrystals,[29] indicating their favourable deposition across the entire TiO_2/Ti_2N MXene surface.

Interestingly, the Ti_2N nanosheets appear partially intercalated among the surface-grown TiO_2 nanoparticles, generating a textured template onto which $CsPbBr_3$ NCs are subsequently anchored. This morphological arrangement is entirely consistent with the structural model illustrated in Figure 8a for NCs@POM-Ti_2N. Such an architecture provides an enlarged interfacial contact area, thereby facilitating efficient charge-carrier migration throughout the heterostructure.

The thermal stability of $CsPbBr_3$ and POM-Ti_2N MXene was investigated using thermogravimetric analysis (TGA) (Figure S8). The results indicate that POM-Ti_2N MXene exhibits high thermal stability, showing only a small percentage of weight loss over the entire temperature range studied. In addition, $CsPbBr_3$ (NCs) shows a sharp weight loss around 600 °C, indicating thermal stability up to this temperature. All of the above indicates the stability of the materials under the catalytic conditions studied.



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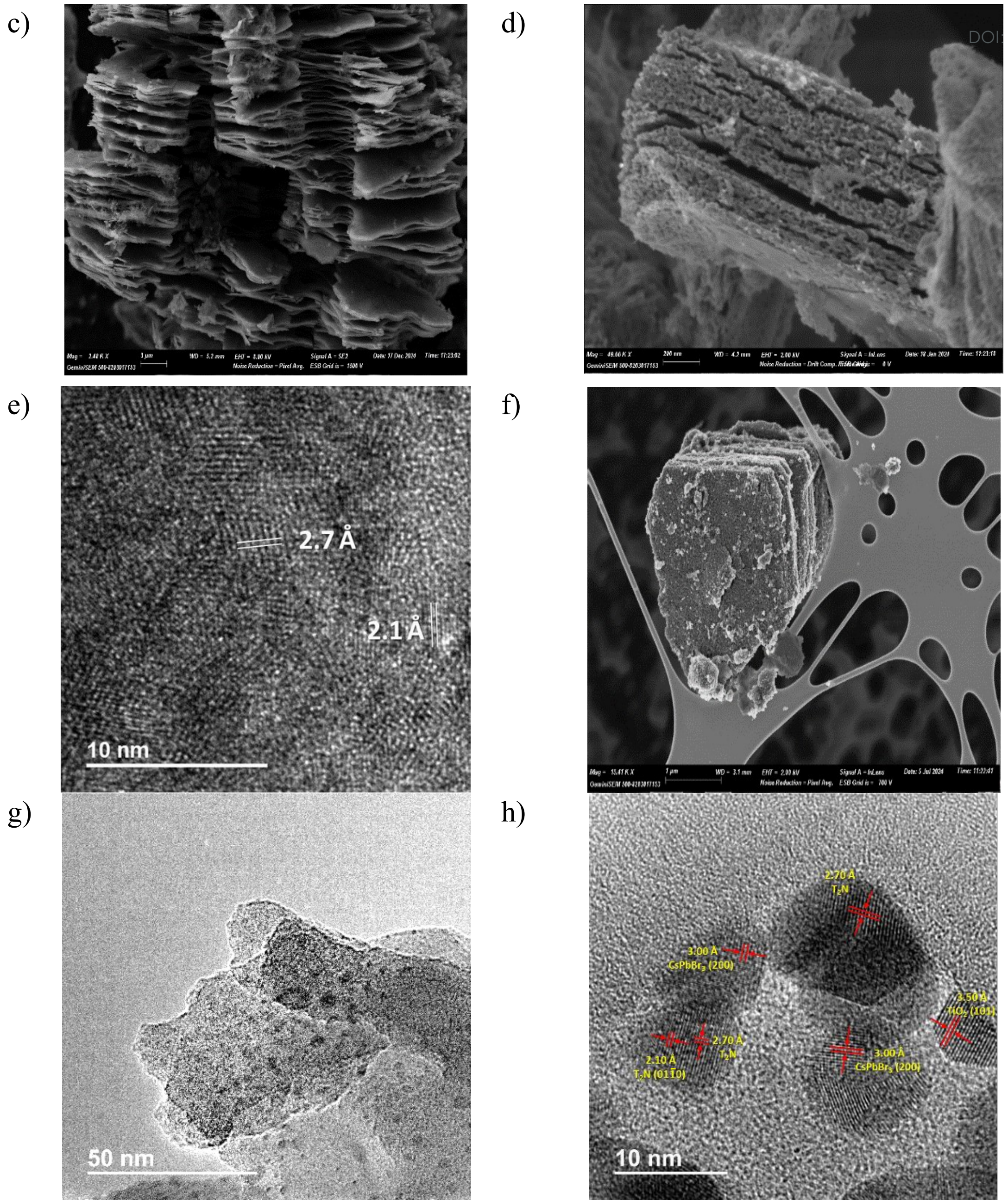

Figure 2. a) HR-TEM image showing the lead halide perovskites ($CsPbBr_3$) nanocrystals. (b) Histogram for the size distribution of the $CsPbBr_3$ NCs, the inset shows enlarged individual NCs, c) HR-FESEM image of Ti_2N MXene, d) HR-FESEM picture of the POM-Ti_2N, e) HR-TEM of a layer of POM-T_2N with different interplanar distances f) HR-FESEM images of the composite NCs@POM-Ti_2N. g) TEM image showing $CsPbBr_3$ NCs distributed across Ti_2O/Ti_2N MXene. h) Corresponding high-resolution (HR-TEM) image of NC@POM-Ti_2N displaying the lattice fringes assigned to anatase TiO_2 (3.50 Å, (101)), Ti_2N MXene (2.70 Å and 2.10 Å, (0110)), and $CsPbBr_3$ nanocrystals (3.00 Å, (200)), confirming the formation of the Ti_2O/Ti_2N heterostructure decorated with $CsPbBr_3$ NCs.

The surface change induced by the partial oxidation of M-Ti_2N produces profound changes in the optical absorption of the material. As shown in Figure S9, when titanium nitride is present, the absorbance spans the UV region to the entire visible range. However, when oxidation occurs, its absorbance becomes significantly more prominent in the UV region up to 380 nm due to the appearance of TiO_2 domains on the M-Ti_2N structure. For the sake of comparison, diffuse reflectance UV-Vis spectroscopy of perovskite NCs, POM-Ti_2N MXene, and composite NCs@POM-Ti_2N are also plotted in Figure 3. Herein, we can see the POM-Ti_2N MXene UV-Vis spectra exhibiting a strong band absorption with an edge at 380 nm, characteristic of TiO_2 absorption. In the case of $CsPbBr_3$ NCs, they display characteristic UV-Vis absorption within the wavelength range of $\lambda < 540$ nm. The UV-Vis spectrum also verifies the formation of the composite NCs and POM-Ti_2N MXene as the supported material combines both absorptions, expanding the photophysical response of the initial POM-Ti_2N in the visible region.

The optical band gaps (E_g) of the synthesized materials were determined using UV-Vis diffuse reflectance spectroscopy (DRS), analyzed through Tauc plot extrapolations (Figure S10, Supporting Information).[30] The extracted band gap values were found to be 2.28 eV[31] for $CsPbBr_3$ NCs and 3.26 eV for the POM-Ti_2N, respectively.

To further elucidate the superior optoelectronic behavior of the perovskite material, the valence band edge positions (E_v^{NHE}) relative to the normal hydrogen electrode (NHE) were investigated using X-ray photoelectron spectroscopy (XPS).[32–34] The E_v^{NHE} values were calculated based on Equation (1):

$$E_v^{NHE} = E_v^{f} + \varphi_{sp} + E_0^{NHE} \tag{1}$$

where E_v^f is the Fermi level of the material determined from XPS measurements, φ_{sp} is the spectrometer work function (4.244 eV), and E_0^{NHE} is the energy level of the standard hydrogen electrode relative to the vacuum level (-4.44 eV).

Based on the calculated valence band (VB) positions and the corresponding optical band gaps, the conduction band minimum (CB) energies were inferred for each material. The estimated VB potentials referenced to the NHE were 1.14 eV for $CsPbBr_3$ NCs and 2.30 eV for POM-Ti_2N, as shown in Figure S11(a, b). Moreover, the CB values of $CsPbBr_3$ NCs and POM-Ti_2N are -1.14 and -0.96 eV, respectively. Regarding the POM-Ti_2N MXene material, we expect two distinct regions: an outer region corresponding to the partially oxidized Ti_2N MXene with TiO_x groups exhibiting electron-withdrawing behavior, and an inner region mainly of Ti_2N MXene with a metallic character, which facilitates efficient electron extraction. Consequently, energy

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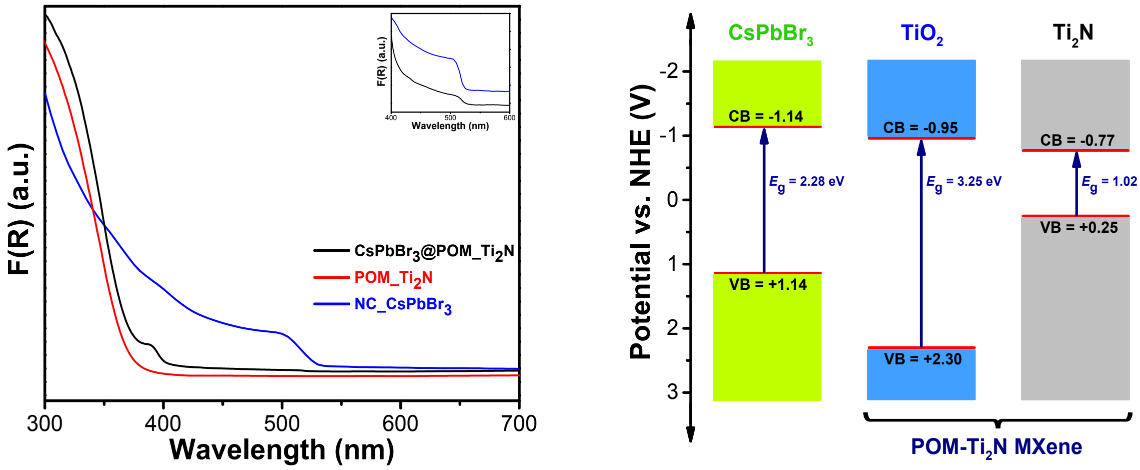
band diagrams were constructed, providing comprehensive insight into the electronic structure of the materials investigated. (Figure 3b)



a) b)

Figure 3. a) Diffuse reflectance UV-Vis optical spectra of $CsPbBr_3$ NCs, Ti_2N MXene and the supported material. The Inset shows a magnification in the characteristic range of the $CsPbBr_3$ NCs absorption. b) Schematic energy band level diagram of each component of $CsPbBr_3$@POM-Ti_2N composite. The respective CB and VB values, as well as the optical band gaps (all in eV), are extracted from the XPS and UV-Vis measurements respectively.

With the aim to understand the mechanism of the catalytic process that occurs during the photo-thermal reaction, steady-state and lifetime emission were studied. The PL spectrum of the $CsPbBr_3$ NCs exhibits a strong emission peak at 530 nm; however, for the sample $CsPbBr_3$@POM-Ti_2N MXene, we observed a decrease in PL intensity along with a blue shift in the peak maximum to 513 nm. This shift to the blue can be attributed to the Burstein-Moss effect[35]. This effect is related to the change in carrier concentration caused by the electronic coupling between the perovskite nanocrystals and the MXene material. In addition, the decrease in emission intensity can be ascribed to the transfer of photogenerated carriers between the $CsPbBr_3$ NCs and the POM-Ti_2N MXene.[36]

The time-resolved fluorescence spectroscopy (Figure 4) was used to investigate the lifetime emission of pure $CsPbBr_3$ NCS and the supported $CsPbBr_3$@POM-Ti_2N MXene catalyst. The best fitting corresponds to a biexponential decay model, where the short lifetime is attributed to nonradiative recombination of electron-hole pairs and surface trap states and the long lifetime to the radiative recombination.[37,38]

The emission lifetime of $CsPbBr_3$@POM Ti_2N MXene (τ_{ave} = 1.73 ns) was relatively shorter than that of the corresponding $CsPbBr_3$ nanoparticles (τ_{ave} = 25.32 ns). This difference in the emission lifetime between both materials indicates the emergence of a nonradiative pathway

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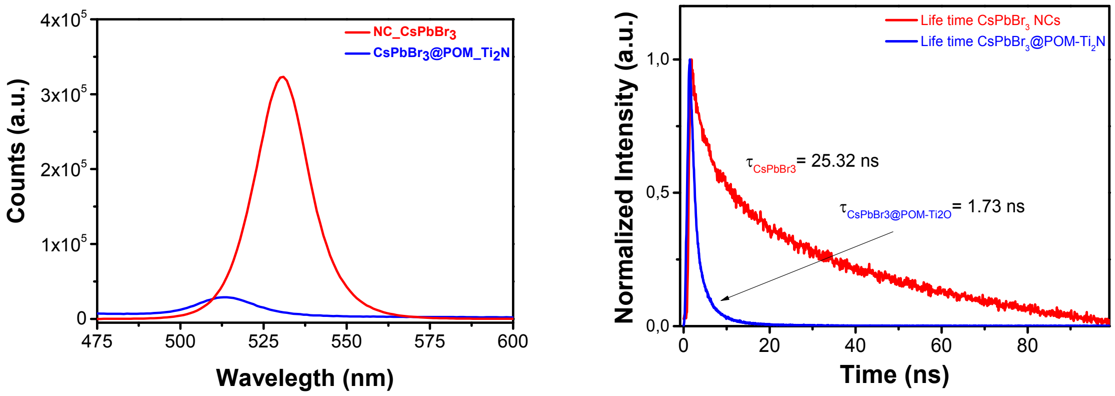
from the significant electronic interaction between $CsPbBr_3$ nanoparticles and partially oxidized MXene.[18] This provides an alternative interfacial pathway for the excited electrons of $CsPbBr_3$ to transfer to the oxidized MXene and relax non-radiatively, allowing them to participate in the catalytic reaction.[35,39]



a) b)

Figure 4. (a) Photoluminescence spectra (λ_{ex} = 405 nm) of $CsPbBr_3$ nanoparticles (red line) and $CsPbBr_3$@POM Ti_2N MXene catalyst (blue line). (b) Lifetime measurements registered at 530 and 513 nm under room conditions of $CsPbBr_3$ nanoparticles (blue line) and $CsPbBr_3$@POM Ti_2N MXene catalyst (red line) respectively. The PL decay lifetimes were calculated to the best fitting to a biexponential decay model ($y = A_1 \cdot e^{-t/\tau 1} + A_2 \cdot e^{-t/\tau 2}$), where A_1 and A_2 correspond to the amplitudes and τ_1 and τ_2 is the lifetime of each component). The average lifetime was calculated using the formula: $\tau_{average} = A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2 / A_1 \cdot \tau_1 + A_2 \cdot \tau_2$.

X-ray photoelectron spectroscopy (XPS) measurements were conducted to determine the chemical states of lead (Pb), bromine (Br), cesium (Cs), titanium (Ti), nitrogen (N) and oxygen (O) in the $CsPbBr_3$ NCs, POM-Ti_2N, and NCs@POM-Ti_2N samples (Figures S12, S13, and S14 show the full survey scans). Figure S12 displays the XPS core spectra for Cs 3d, Pb 4f, and Br 3d states, respectively, calibrated using the adventitious C 1s peak set to a binding energy (BE) of 284.8 eV.[40] In the case of $CsPbBr_3$ NCs, the BE peaks for Cs 3d at 724.0 and 738.0 eV correspond to the Cs $3d_{5/2}$ and Cs $3d_{3/2}$ signals (Figure 5a) while the Pb 4f spectrum shows two peaks at 138.0 and 142.9 eV, attributed to the Pb $4f_{7/2}$ and Pb $4f_{5/2}$ levels respectively, of the Pb^{2+} state, consistent with previous literature reports.[41,42] (Figure 5b) Additionally, two Br 3d peaks are observed at 67.9 and 69.0 eV, corresponding to Br $3d_{5/2}$ and Br $3d_{3/2}$ contributions.[43,44] (Figure 5c) Further examination of the Ti 2p spectrum for the NCs@POM-Ti_2N composite reveals that the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels corresponding to Ti-N in POM-Ti_2N appear at BE values of 458.5 and 464.2 eV, respectively. The Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels associated with Ti-

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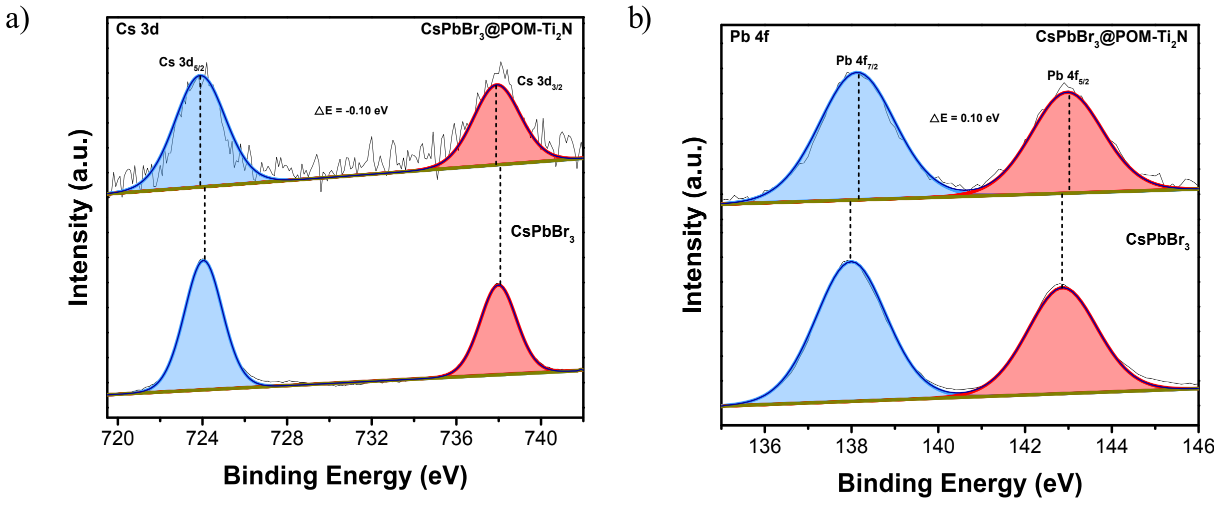
O bonds characterize the POM-Ti_2N MXene, with various oxidation states from Ti^{2+} to Ti^{4+} presenting at BE values around 455.7 - 459.8 and 461 - 466 eV, respectively.[45,46] (Figure 5d) Further evidence of the formation of the composite NCs@POM-Ti_2N is found in the XPS spectrum shown in Figure 5, which analyses the elemental XPS signals of $CsPbBr_3$ and POM-Ti_2N MXene before and after formation of the composite. Due to the effective formation of an interface between perovskites and POM-Ti_2N MXene, subtle shifts in the Pb, Br, Ti, and N peak positions are observed, as shown below. Specifically, the binding energies for Pb 4f and Br 3d in the NCs@POM-Ti_2N composite shift towards more positive values, indicating a reduction in electron density on $CsPbBr_3$.[47] Conversely, the binding energies assigned to Ti 2p and N 1s (from Ti-N bonding) exhibit a negative shift, suggesting an increase in electron density on the POM-Ti_2N MXene particles (Figure 5d, e).[48] The Ti 2p spectrum of the NCs@POM-Ti_2N composite shows a clear shift of the main peak positions to lower BE values compared to POM-Ti_2N MXene alone, indicating a chemical interaction between the perovskite nanocrystals and the POM-Ti_2N MXene structure.

In addition, despite partial oxidation of the nitride MXene, Ti-N bonds characteristic of titanium nitride predominates, as evidenced by Ti $2p_{3/2}$ and Ti $2p_{1/2}$ signals at binding energies of approximately 458.5 eV and 464.2 eV, respectively. Additionally, the presence of an N 1s signal around 399.5 eV confirms the continued existence of N-Ti bonds,[49,50] and the peak at 400.8 eV may be associated with nitrogen atoms in the Ti(N, O) oxynitride lattice. (Figure 5e) These findings indicate that, although some surface oxidation occurs, forming TiO_2, the internal structure of POM-Ti_2N predominantly retains its titanium-nitride bonds, thus facilitating an effective electronic interaction with the $CsPbBr_3$ nanocrystals. In summary, all these observations support the notion of electronic interaction between the orbitals that form $CsPbBr_3$ NCs and POM-Ti_2N MXene.



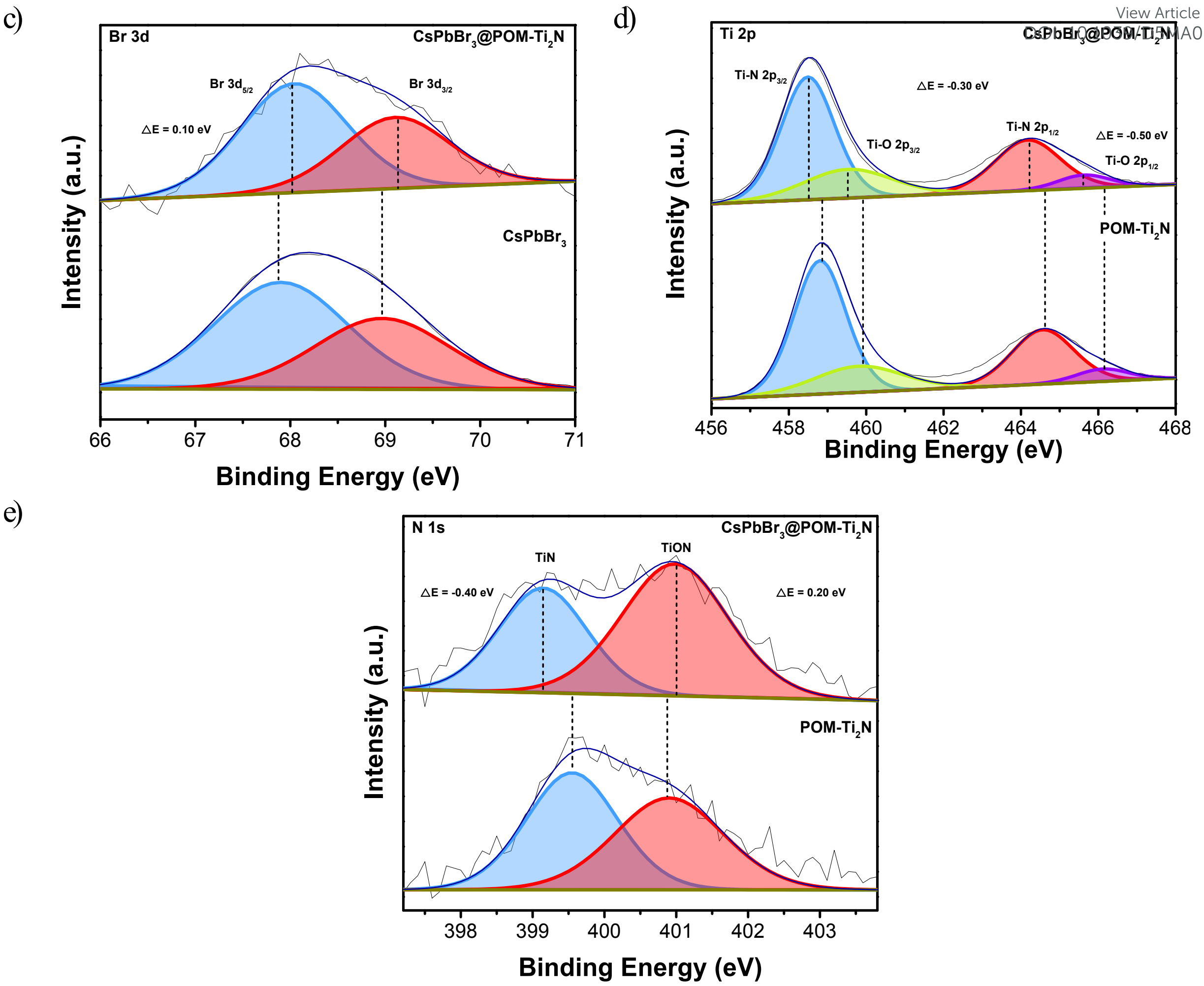


Figure 5. XPS spectra of CsPbBr$_3$ NCs, POM-Ti$_2$N (bellow), and NCs@POM-Ti$_2$N composites (top): a) Cs 3d spectra, b) Pb 4f spectra, c) Br 3d spectra, d) Ti 2p spectra, and e) N 1s spectra.

To investigate the reducibility and metal–support interactions within the hybrid, H_2 temperature-programmed reduction (H_2-TPR) measurements were conducted (Figure 6a). Pure TiO_2 exhibits only a weak, broad reduction event centred at ~535 °C,[51] characteristic of kinetically hindered lattice-oxygen removal and indicative of strongly bound oxygen species with low surface mobility. A similar trend has been observed for TiO_2 nanosheets by other authors.[52] Conversely, the POM–Ti_2N composite exhibits a markedly different H_2 consumption behavior, revealing two pronounced low-temperature reduction peaks with maxima centered at 314 °C and 381 °C. The presence of these features at significantly lower temperatures reflects the formation of highly labile surface oxygen species generated at the Ti_2N/TiO_2 interface.[53] According to the reducibility criterion, where lower peak temperatures correspond to more weakly bonded oxygen species such as O^-/O^{2-},[54] these events confirm the emergence of readily accessible active oxygen centres not present in pristine TiO_2. This enhanced reducibility is attributed to a strong metal-support interaction (SMSI) between the almost conductive Ti_2N

core and the ultrathin surface-oxidised TiO_2 shell.[55] The Ti_2N framework promotes electron donation, activating H_2 molecules and facilitating the formation of hydrides, which collectively weakens the surface Ti-O bonds and triggers stepwise reduction of the MXene surface. Concurrently, the high-temperature feature centred at ~530 °C originates from the reduction of oxidised TiO_2 moieties anchored on the POM surface, consistent with the consumption of more strongly bound lattice oxygen. Taken together, these redox characteristics demonstrate that the POM–Ti_2N hybrid possesses substantially improved oxygen lability and electronic coupling compared to pristine TiO_2. Such behaviour is essential for catalytic activation, as the generation of easily reducible oxygen species and the formation of a robust Ti_2N-TiO_2 heterojunction provide the active environment required for efficient H_2 dissociation, CO_2 adsorption, and subsequent photothermal reduction to CO and CH_4.

Furthermore, the CO_2 adsorption behaviour of POM-Ti_2N and TiO_2 was further examined by CO_2 temperature-programmed desorption (CO_2-TPD), as illustrated in Figure 6b. POM–Ti_2N and TiO_2 exhibit a desorption peak in the low-temperature region (~105 ºC),[56] which can be attributed to physisorbed CO_2 weakly interacting with surface hydroxyl groups. In the case of TiO_2, this low-temperature feature dominates the profile, indicating a limited population of strongly adsorbed carbonate species.[57] In contrast, POM–Ti_2N displays a markedly enhanced desorption signal extending into the high-temperature region (350 - 700 ºC), with a pronounced maximum centred at approximately 525 °C. This peak reflects the formation of strongly bound carbonate species, resulting from the interaction of CO_2 with basic surface sites generated during the formation of the TiO_2 moieties within the POM–Ti_2N heterostructure. The significantly increased desorption intensity suggests an enlarged density of active sites capable of stabilising chemisorbed CO_2 species. These results collectively indicate that the incorporation of Ti_2N and its partial oxidation to TiO_2 enhances both the strength and capacity of CO_2 adsorption.

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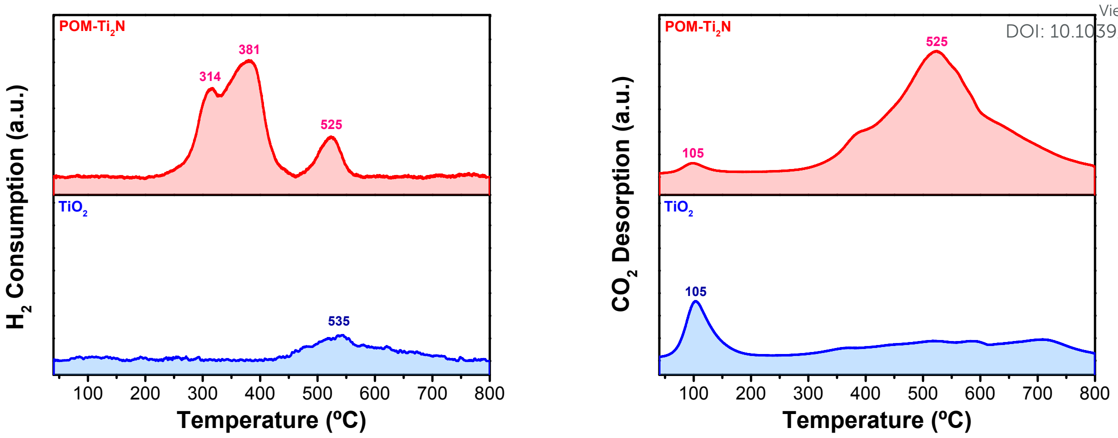

a) b)

Figure 6. a) H_2-TPR analysis profiles of the tested materials: POM-Ti_2N (red line) and TiO_2 (blue line). b) CO_2-TPD profiles obtained on POM-Ti_2N (red line) and TiO_2 (blue line) materials. In both studies, the ramp rate was 10ºC·min^{-1}.

Periodic DFT calculations were performed with VASP (PAW-PBE including dispersion corrections;[58,59] full computational details are provided in the Supporting Information) on three representative Ti-based supports designed to mimic the POM-Ti_2N composite: a Ti_2N MXene monolayer (conductive nitride core), a rock-salt TiN(100) slab (nitride surface), and rutile TiO_2 (110) surfaces with and without a surface oxygen vacancy, V_O (partially oxidized TiO_2/TiO_x domains) (Figure S15). CO_2 and H_2 were individually adsorbed at low coverage on each model, exploring several initial geometries. Among these, Ti_2N exhibited the largest thermodynamic affinity for CO_2 (E_{ads} = -3.32 eV),[60,61] whereas stoichiometric TiO_2(110) bound CO_2 only weakly (E_{ads} = -0.10eV), in line with previous DFT and surface-science studies.[62,63] Introducing a surface oxygen vacancy on TiO_2(110) markedly strengthened CO_2 adsorption (E_{ads} = -1.11 eV) and led to bent, vacancy-anchored configurations, consistent with the enhanced reactivity of defective rutile surfaces.[64–66] In contrast, molecular H_2 adsorption was found to be very weak on all Ti-based supports ($|E_{ads}(H_2)| \leq 0.05$eV), while an artificially initialized, dissociated H_2 state on Ti_2N was strongly stabilized (E_{ads} = -7.57eV per H_2), indicating that nitride sites act as a deep thermodynamic sink for atomic hydrogen rather than as strong chemisorption sites for molecular H_2.[67] Taken together with the H_2-TPR and CO_2-TPD data, these DFT trends support a bifunctional picture in which oxygen-deficient TiO_2/TiO_x regions and TiO_2/Ti_2N interfacial sites provide the main CO_2-binding and activation centres, whereas the TiN/Ti_2N scaffold supplies electronic/photothermal conductivity and preferentially stabilizes dissociated hydrogen species, as described in detail in the DFT analysis (see Supporting Information).

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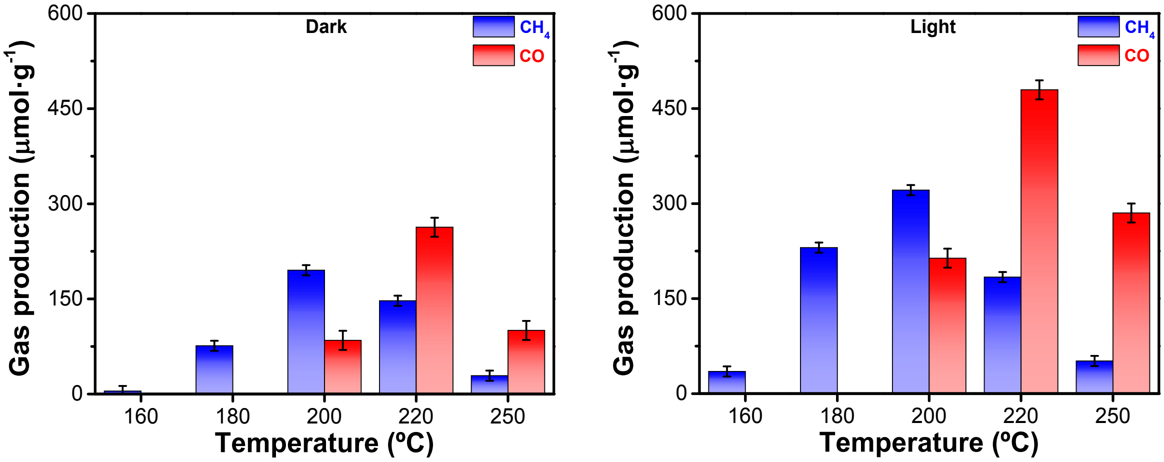
Catalytic Activity of the NCs@POM-Ti_2N material

First, the catalytic activity of NCs@POM-Ti_2N was studied in temperatures ranging between 160 to 250 °C, either in the dark (thermal catalysis) or under light irradiation (photo-thermal catalysis). Figures 7, S16 and S17 summarizes the catalytic results obtained under light and dark conditions. In both cases, under light or dark, at low temperatures selectivity towards CH_4 is 100% but as temperature increases selectivity shifts to CO. Additionally, maximum conversion is achieved above 200 ºC whereas at 250 ºC the activity drops. This fact can be due to changes happening on the support as the colour of POM-Ti_2N shifted from light grey to dark grey at these temperatures. On the other hand, as shown in Figure 7, under light irradiation production of CO_2-derived products is always higher compared to dark. These differences in the catalytic activity indicate that CO_2 conversion in NCs@POM-Ti_2N light effectively assists the reaction.

A deeper analysis of catalytic data summarized in Table 1 brings further arguments for the photo-thermal catalytic pathway, especially, which is more evident at lower temperatures. A comparison of CO_2 conversion or CH_4 production at temperatures of 160 ºC or 180 ºC leads to conversions 5 to 4-fold higher when photo-thermal conditions are applied. Interestingly, both thermal and photothermal conditions share similar trends displaying higher conversions at 220 ºC, in both cases, CO production starts at 200 ºC and has a gaussian plot in which 220 ºC seems to be the most active temperature conditions. It seems that at higher temperatures than 180 ºC desorption of reaction intermediates is favored difficulty the complete hydrogenation of CO_2 to CH_4.



a) b)

Figure 7. Photocatalytic activity for $CsPbBr_3$(5 wt%)@POM-Ti_2N MXene under different conditions of temperature (a) in the dark, (b) under light irradiation. Reaction conditions: $CsPbBr_3$(5 wt%)@POM-Ti_2N MXene (10mg), P_{H2} = 1.2 bar, P_{CO2} = 0.3 bar, at 23h reaction time, simulated sunlight irradiation (226 mW·cm^{-2}), and temperature as indicated.

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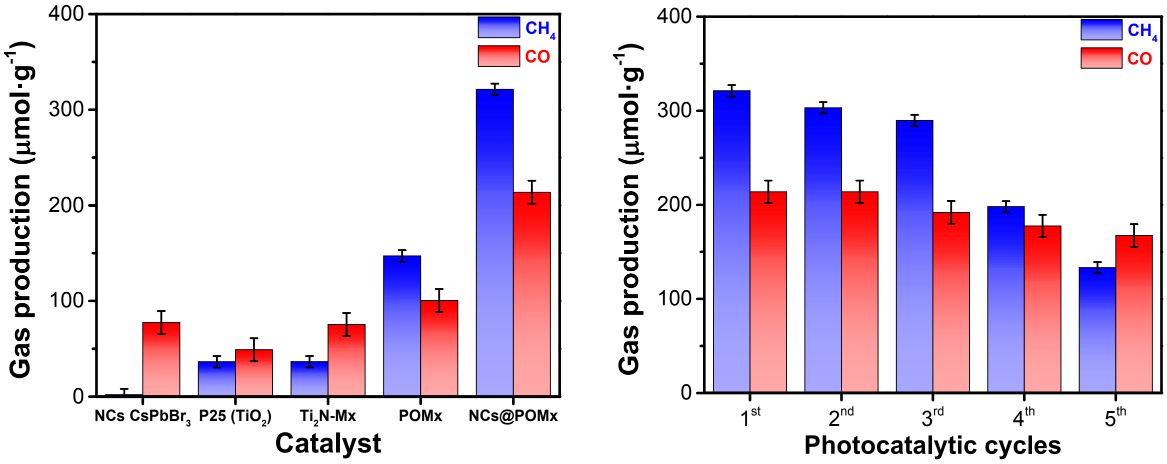
Table 1. Comparison of CH_4 and CO selectivity of $CsPbBr_3$(5 wt %)@POM-Ti_2N MXene at different temperatures and conditions (dark or light).

T. Reaction (ºC)	Condition	Selectivity CH_4 (%)	Selectivity CO (%)
160	Dark	100	0
	Light	100	0
180	Dark	100	0
	Light	100	0
200	Dark	70	30
	Light	60	40
220	Dark	36	64
	Light	28	72
250	Dark	22	78
	Light	15	85

For comparison, we studied the photo-thermal activity for CO_2 reduction using $CsPbBr_3$ nanocrystals and $CsPbBr_3$@POM-Ti_2N MXene at 200°C. (Figure 8). As can be seen, our $CsPbBr_3$@POM-Ti_2N catalyst presents the highest activity for CH_4 production compared to pristine $CsPbBr_3$ NCs or POM-Ti_2N MXene alone. In fact, while the components of the composite $CsPbBr_3$ and M- Ti_2N MXene are not as active as the pristine POM- Ti_2N we assume the catalytically active sites are present in the oxidized side of the POM- Ti_2N. (Figure 8a) However, selectivity changes occurred when POM-Ti_2N is loaded with the perovskite due to the suppression of CO production and a change of selectivity towards CH_4. This indicates a synergistic effect between both materials when they form a combined material.



a) b)

Figure 8. a) Comparison of photocatalytic activity for different samples. b) Recycling of the photocatalyst $CsPbBr_3$(5 wt%)@POM-Ti_2N MXene. Reaction conditions: Photocatalyst (10mg), P_{H2} = 1.2 bar, P_{CO2} = 0.3 bar, at 23h reaction time, simulated sunlight irradiation (226 $mW\cdot cm^{-2}$), and 200 °C.

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In addition, the recyclability of $CsPbBr_3$@POM-Ti_2N MXene was evaluated over five consecutive cycles under identical reaction conditions, as illustrated in Figure 8b. The results indicate a stable CH_4 production yield for the first three cycles (only a 3% reduction in activity per cycle), suggesting desirable photostability of the catalyst, even with each cycle lasting 23 hours. Interestingly, while CH_4 remained the primary product, CO was observed as a byproduct of the reaction. We attribute this emergent CO formation to surface restructuring and the gradual alteration of active sites, likely due to subtle changes in the surface composition or morphology of the $CsPbBr_3$@POM-Ti_2N during the initial reaction cycle. This shift in selectivity, with CO generation emerging, may be explained by changes in the binding and activation of CO_2 at newly exposed or modified active sites on the catalyst surface. This argument get reinforced since XPS data shown in Figure 5 reveals the electronic polarization in Cs and Ti atoms after the formation of $CsPbBr_3$@POM-Ti_2N, suggesting that perovskite NCs are not randomly deposited, if not interacting somehow. Photocatalytic CO_2 reduction involves a series of complex, multi-step processes, including light absorption, charge separation, reactant adsorption, and catalytic reduction at active sites.[68] Minor modifications in any of these steps—particularly in the structure of surface-active sites can significantly impact product selectivity. In this case, MXene support likely plays a dual role: enhancing electron-hole separation and simultaneously protecting $CsPbBr_3$ nanocrystals from rapid degradation, as confirmed by the absence of notable changes in XRD patterns (Figure 1, black line) and consistent XPS spectra. Nevertheless, with continued cycling, slight restructuring of the surface may expose new catalytic sites that favor CO production. By the fourth cycle, a reduction of approximately 30% in CH_4 yield was observed, possibly due to gradual surface degradation or partial deactivation of active sites, while CO production remained stable. This indicates that, despite a decrease in CH_4 yield, the modified surface continues to facilitate CO_2 reduction to CO, suggesting persistent reactivity at specific catalytic sites that favor CO production over CH_4. In fact, while $CsPbBr_3$@POM-Ti_2N has higher selectivity towards CH_4, their individual components (M-Ti_2N MXene, POM-Ti_2N MXene, and $CsPbBr_3$ nanocrystals) are also selective to CO. This change in catalytic activity agrees with superficial chemicophysical changes on POM-Ti_2N surface. This matches with the observation made in the XPS in terms of electronic densities of atomic elements that compose $CsPbBr_3$ NCs and the POM-Ti_2N. These findings underscore the importance of optimizing both the initial surface properties and long-term stability of active sites to maintain selective CO_2 photoreduction over extended reaction cycles.

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Proposed mechanism (Photocatalytic CO_2 Reduction)

According to XPS and UV-Vis measurements, the energy alignments of CB and VB of $CsPbBr_3$ NCs, POM-Ti_2N, and $CsPbBr_3$@POM-Ti_2N were calculated. From a thermodynamic point of view, the reduction of CO_2 to CO and CH_4 in all cases, see Figure 9b. However, CO_2 conversion increases in a considerable way in the case of the $CsPbBr_3$@POM-Ti_2N composite, specially upon UV-Vis light exposure. This fact, plus the intrinsic heterojunction morphology of the composite (see Figure 9a) suggests that photogenerated electrons can flow from the conduction band (CB) of the perovskite to the CB of the TiO_2 layer that eventually will pass to the Ti_2N. Thus, inducing effective charge separation enabled by a type II heterojunction formed between the $CsPbBr_3$ NCs and the POM-Ti_2N MXene structure. Additionally, the difference in potential between the two materials generates an internal electric field (IEF) that further enhances charge separation and transfer efficiency.[69] The direction of the IEF may be proved by XPS results (Figure 5).

The TiO_2 layer also reduces direct recombination between the perovskite and the MXene, forming an additional small electric field that promotes electron flow into the MXene and avoids recombination. The introduction of such an interlayer to reduce direct recombination is a well-known strategy in the field of dye-sensitized solar cells (DSSCs) and hybrid solar cells.[70,71]

Thus, these electrons that are injected to the MXene can reduce CO_2 into either CO or CH_4 through multielectron transfer pathways:[72]

$$\mathrm{CO_2} + 2\mathrm{H^+} + 2e^- \rightarrow \mathrm{CO} + \mathrm{H_2O} \qquad (E^0{}_{redox} = -0.53V) \tag{2}$$

$$\mathrm{CO_2} + 8\mathrm{H^+} + 8e^- \rightarrow \mathrm{CH_4} + 2\mathrm{H_2O} \qquad (E^0{}_{redox} = -0.24V) \tag{3}$$

Moreover, these reactions proceed concurrently, with their predominance governed by the interplay between thermodynamic feasibility and kinetic accessibility. Thermodynamically, the formation of CH_4 is favored; however, kinetically, CO production is more accessible as it requires fewer electrons ($2e^-$ vs. $8e^-$ for CH_4). Experimental data from Table 1 and Figure 7 confirm this duality. At lower temperatures (160 - 180 °C), CH_4 selectivity remains at 100%, indicating a thermodynamically driven process. However, as the temperature increases (200 - 250 °C), a significant shift in selectivity toward CO is observed, dropping CH_4 selectivity to 15% under illumination at 250 °C. These results suggest that at higher reaction temperatures, kinetic factors increasingly govern product distribution.

Therefore, the temperature-dependent behavior observed in the $CsPbBr_3$@POM-Ti_2N composite under light irradiation illustrates a nuanced balance between thermodynamics and kinetics.[73]

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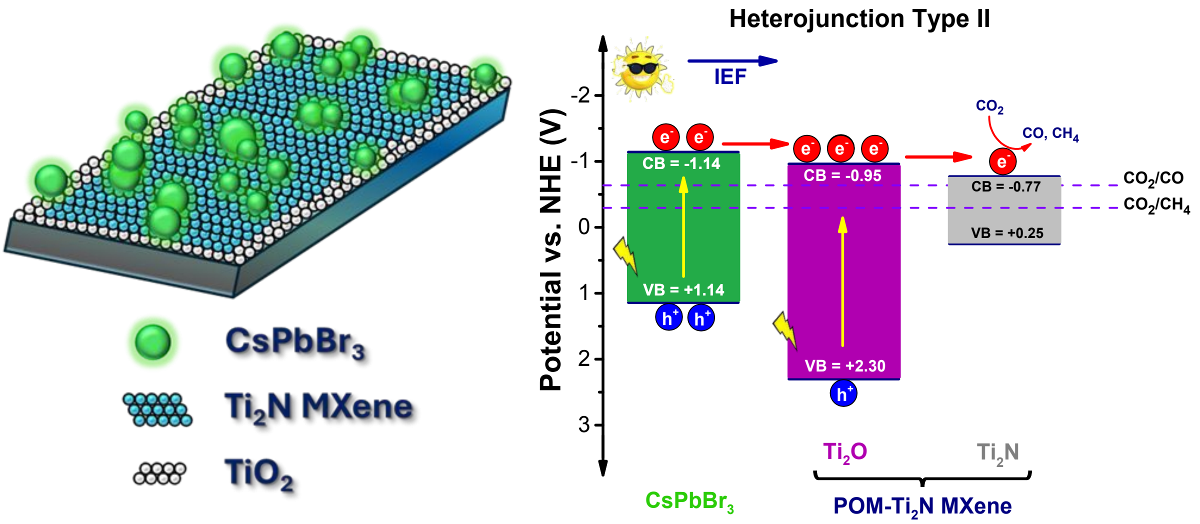
In summary, the superior photocatalytic activity of $CsPbBr_3$@POM-Ti_2N can be attributed to several synergistic factors. First, the composite exhibits enhanced light absorption across the visible spectrum compared to the individual components (Figure 8a), generating more charge carriers. Second, the heterojunction architecture suppresses electron-hole recombination, thereby ensuring greater availability of charge carriers for surface redox reactions. Lastly, the 2D/0D structural configuration—where zero-dimensional $CsPbBr_3$ NCs are uniformly distributed over a two-dimensional layers of POM-Ti_2N support—maximizes active surface area and facilitates efficient interfacial charge migration. (Figure 9)



a) b)

1. Upon illumination, the perovskite absorbs photons, generating electron-hole pairs.
2. Internal electric fields (IEF) push electrons toward TiO_2 and then to MXene.
3. Electrons accumulate at the MXene surface, where they reduce CO_2 to CO and CH_4.

Figure 9. a) The schematic diagram of $CsPbBr_3$@POM-Ti_2N composite. b) Diagram of CH_4 and CO production by $CsPbBr_3$@POM-Ti_2N composite system under sunlight irradiation and charge migration and separation.

3. Conclusions

In conclusion, this study highlights the successful synthesis and performance of a novel hybrid heterojunction composed of $CsPbBr_3$ nanocrystals supported on partially oxidized Ti_2N MXenes (POM-Ti_2N), specifically engineered for efficient photo-thermal CO_2 conversion into CH_4 and CO. Preparation of the hybrid material was achieved through by simple ultrasonic impregnation, enabling the uniform deposition of $CsPbBr_3$ NCs onto the surface of the 2D POM-Ti_2N sheets. The partial oxidation of Ti_2N was fundamental to introducing oxygen-containing functional groups, which improved surface hydrophilicity and provided anchoring sites for the nanocrystals. This facilitated strong interfacial interactions, critical for enhancing the overall photocatalytic activity.

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The proposed mechanism involves a synergistic interplay between light absorption, charge separation, thermodynamic, and kinetic effects. $CsPbBr_3$ NCs serve as efficient light harvesters due to their strong absorption in the visible range and excellent charge transport properties. Upon irradiation, electron–hole pairs are generated in the perovskite, with electrons being efficiently transferred to the POM-Ti_2N support. The partially oxidized MXene acts both as a photothermal catalyst and an electron sink, avoiding charge recombination to promote the catalytic reduction of CO_2, while simultaneously accelerating charge separation and transport. The presence of oxygen vacancies and various oxidation states from Ti^{2+} to Ti^{4+} on the POM-Ti_2N surface further facilitates CO_2 adsorption and activation, which are essential for driving the CH_4 and CO formation pathway with high selectivity.

In terms of recyclability, the hybrid catalyst demonstrated excellent structural integrity, maintaining its catalytic activity over multiple reaction cycles. Post-reaction analyses showed minimal degradation of the $CsPbBr_3$ NCs, retaining the interfacial architecture and confirming the robustness of the catalyst under operational conditions. Overall, the $CsPbBr_3$@POM-Ti_2N hybrid catalyst demonstrates a promising strategy for the design of stable and highly active photocatalysts, combining the tunable optoelectronic properties of perovskite NCs with the multifunctionality of 2D MXenes. The enhancement in CH_4 and CO production under light-driven conditions underscores the potential of this hybrid catalyst in advancing solar-to-fuel technologies.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

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The data supporting the results of this study are available from the corresponding author upon reasonable request.