



Coupling TiO₂ with Nb carbide-based materials for H₂ photoproduction: From 3D carbides to 2D MXenes[☆]

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ABSTRACT

In this work we coupled 3D Nb carbide, ternary layered NbMAX, and 2D NbMXene with TiO₂, developing new photocatalysts for the renewable H₂ production from ethanol aqueous solutions. A new preparation method of Nb₂CT_x MXene is reported; the hydrothermal method proposed uses NH₃(aq) and avoids the utilization of hazardous HF or a strong acid and fluoride salts. After thorough characterization of the structural and physico-chemical features of the materials, their photocatalytic performance has been related to their photo-electrochemical properties. Moreover, the interaction of the reactant molecules with the TiO₂-based composites and their evolution under UV irradiation has been investigated by *in situ* IR spectroscopy. All composites showed a higher H₂ production rate and a higher lifetime of photogenerated charges (h⁺/e⁻) than TiO₂. The Nb₂CT_x-containing photocatalyst showed the best H₂ production yield, both in gas and liquid phase, owing to a very efficient transfer of the photogenerated electrons from the TiO₂ conduction band to the MXene phase, decreasing the rate of charge recombination and favoring the H₂ formation. The H₂ production of NbMXene/TiO₂ was more than 3.5 times that of TiO₂ and showed a stable behavior at least up to 7 h with light on/light off cycles.

1. Introduction

Nowadays hydrogen is proposed as a clean energy vector to favor the decarbonization of the energy mix. However, hydrogen is still mainly produced from fossil sources and huge efforts have been devoted to moving to green H₂, which can be obtained from water electrolysis using renewable electricity. For a more diversified green H₂ production in the medium to long term, other sources and/or routes should be considered, including photocatalytic approaches [1,2]. In this field, the use as sacrificial electron donors of biomass-derived substrates, such as bio-alcohols, which are currently produced by well-established routes, could help to achieve a more efficient photocatalytic production of sustainable H₂ [3–5]. Moreover, other valuable products can be obtained from the organic substrate, further enhancing the process's appeal from an environmental point of view [6].

Many investigations have been focused on the use of TiO₂ as semiconductor in photocatalytic processes, some of them studying how to

improve its performance by controlling its morphology, particle size, and surface properties; among the different TiO₂ polymorphs, anatase is the most widely employed in photocatalysis [7,8]. One of the strategies followed for the application of TiO₂ in photocatalytic H₂ production, has been its coupling with noble metals co-catalysts, which decreases the H₂ evolution overpotential and the h⁺/e⁻ recombination rate [9,10]. 3D transition metal carbides (TMCs) have also been investigated as a cheaper alternative, since they display catalytic properties similar to Pt-group elements [5,11,12]. Nowadays, besides 3D TMCs, MAX phases and MXenes are also attracting increasing attention in photocatalysis, owing to their interesting features arising from their lamellar structure and their peculiar electronic properties [13–16]. These materials exhibit a combination of ceramic and metal properties, showing high thermal and electrical conductivity, with a catalytic behavior that, in some cases, can be compared to that of noble metals [17]. In particular, MAX phases are hexagonal ternary layered materials, where M is an early transition metal, A represents elements from groups 11–16, such as Al, Si or Ga,

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and X represents carbon or nitrogen [18]. Starting from a MAX compound, the corresponding MXene phase can be obtained by selective etching of the A atomic layers leading to 2D materials with unique and tunable electronic, optical, mechanical, and electrochemical properties [19,20]. These peculiar features have increased the current interest in the study of MAX synthesis and properties [17,21].

The use of HF, or fluoride salts in the presence of HCl, are the most common methods for etching in MXene preparation. However, due to concerns regarding the use or generation of HF, other methods have been explored, with the etching of Ti_3AlC_2 MAX being the most studied [22,23]. Among these methods, the treatment with NaOH under hydrothermal conditions, or with organic bases, such as tetramethylammonium hydroxide, and ultrasounds, have been shown to produce the corresponding MXene and $[\text{Al}(\text{OH})_4]^-$ [22,23].

Besides Ti-based MXenes, other MXenes, such as Nb_2C , have also attracted much attention, mainly due to their suitable properties for application in diverse energy storage and conversion technologies [24,25]. Nb_2C , with a lower Fermi level than Ti_3C_2 [26], has been proposed as a good candidate to be coupled with a semiconductor and be used as cocatalyst [15,24,27]. However, a limited number of studies have been carried out in the photocatalytic H_2 production using Nb_2C [28–30].

This background inspired us to explore a new preparation method for Nb_2C MXene from Nb_2AlC MAX phase. Thus, here we report for the first time, the etching of Nb_2AlC by means of a hydrothermal treatment with $\text{NH}_3(\text{aq})$ to obtain Nb_2CT_x ($T = \text{O}, \text{OH}$ surface terminations) MXene. In addition to Nb_2C MXene, other niobium carbides such as 3D NbC and Nb_2AlC MAX phase could be also appropriate co-catalysts for TiO_2 . Then, in this work we prepared a set of TiO_2 -based composites, containing 3D NbC, Nb_2AlC MAX phase, and Nb_2CT_x MXene. The goal of this work is the study of these materials in the photocatalytic H_2 production from aqueous ethanol, comparing the characteristics of the different materials and the role as co-catalyst of the different Nb carbides.

The textural, morphological and structural characteristics of all the prepared composite materials (NbC/TiO_2 , $\text{NbMAX}/\text{TiO}_2$ and $\text{NbMXene}/\text{TiO}_2$), as well as their photoelectrochemical properties, were carefully assessed combining different techniques. The influence of the presence of ethanol in the photocurrent response and in the resistance to the charge transfer was additionally ascertained. Moreover, an *in situ* infrared spectroscopy study was performed to study, at the molecular level, the interaction of the reactants with the photocatalyst surface and the evolution of the systems under UV irradiation; this study also allowed to determine for the different photocatalysts, in the presence of ethanol, the differences in the lifetime of the photogenerated charges. Finally, the characteristics of the new materials are successfully related to their photocatalytic performance in H_2 production from aqueous ethanol in both gas and liquid phase.

2. Experimental

2.1. Materials synthesis

Nb carbides-based/ TiO_2 composites (Nb wt% ~3) were prepared by an ultrasonic-assisted method [5], using a SONICS VCX 500 equipment, from ethanol suspensions of NbC, Nb_2AlC or Nb_2CT_x co-catalysts and commercial anatase TiO_2 (Thermo Fisher Sci., 99.6 %, BET specific surface area = $8 \text{ m}^2 \text{ g}^{-1}$). The catalysts were labelled NbC/ TiO_2 , NbMAX/ TiO_2 and NbMXene/ TiO_2 . NbC was synthesized using a previously reported method [31]. Nb_2AlC used was commercial (Forsman Scientific, 95 % purity). As stated above, the material containing Nb_2CT_x was prepared by etching Nb_2AlC under hydrothermal conditions using $\text{NH}_3(\text{aq})$. For such purposes, MAX Nb_2AlC (500 mg) was firstly ball-milled and then mixed with 50 mL of a 13 M $\text{NH}_3(\text{aq})$ solution. After that, the mixture was introduced in an autoclave equipped with a 75 mL Teflon vessel; the system was purged with Ar several times to displace

air and, finally, pressurized with Ar up to 3.5 bar at room temperature. Afterwards, the temperature was increased up to 200°C ($20^\circ\text{C}/\text{min}$) and kept 24 h. Next, the system was left to cool at room temperature and gently depressurized. Then, the solid was allowed to settle and the supernatant liquid separated. The obtained solid was subsequently washed repeatedly with acetone/water (10 % v/v) and finally centrifuged multiple times until the pH of the washing solution became neutral.

2.2. Physico-chemical and electrochemical characterization

The specific surface area (S_{BET}) was determined using a QUADRASORB evo™ apparatus. Niobium content was quantified using an Epsilon 3 X-ray fluorescence (XRF) energy-dispersive spectrophotometer from PANalytical; appropriate Nb calibration standards were used. X-ray diffraction (XRD) was performed with a PANalytical X'Pert PRO MPD Alpha1 diffractometer using $\text{Cu K}\alpha$ radiation. Raman spectroscopy was conducted in a Jobin-Yvon LabRaman HR 800 spectrometer with a 532 nm Torus (Laser Quantum) Diode-Pumped Solid State (DPSS) green laser and with a dispersive grating of 600 lines/mm. Infrared (IR) spectra of co-catalysts were acquired with an ATR-diamond ThermoFischer iS5 spectrometer. UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) was realized with a Shimadzu UV 3600 UV-Vis/NIR equipment using BaSO_4 as reference. Scanning electron microscopy (SEM) analysis was performed on a FESEM JEOL J-7100 scanning electron microscope, equipped with an EDX detector, under an accelerating voltage up to 20 kV. Transmission electron microscopy (TEM) experiments were performed in a JEOL J2010F microscope, equipped with a Schottky field emission gun (FEG) and operated at an accelerating voltage of 200 kV. Images were recorded using a Gatan Orius CCD camera. The X-ray photoelectron spectroscopy (XPS) experiments were carried out in an ESFOSCAN equipment based on the PHI VersaProbe 4 instrument from Physical Electronics (ULVAC-PHI) with monochromatic 1486.6 eV Al $\text{K}\alpha$ radiation, calibrated using the $3d_{5/2}$ line of Ag. Measurements are referenced to the C 1s signal at 284.8 eV of adventitious carbon. The analysis was performed using MultiPak software, and the fitting of the spectra was made with CasaXPS program. All measurements were carried out in an ultra-high vacuum chamber at a pressure between 5×10^{-10} and 5×10^{-9} Torr, without any sample pretreatment. Photoluminescence spectroscopy (PL) was performed at room temperature using a Jobin-Yvon LabRam HR 800 spectrometer, with a laser He-Cd (Kimmon Koha IK3201R-F), coupled to an optical microscope Olympus BXFM (40x NUV microscope objective); the CCD detector was cooled at -70°C . The laser line used was 325 nm and the dispersive grating was 300 lines/mm. For the photoelectrochemical characterization of samples, the photocurrent response and the electrochemical impedance spectroscopy (EIS) measurements were performed using a VMP3, BioLogic Science Instruments setup at ambient conditions. The equipment consists of a computer-controlled potentiostat with an undivided three-electrode cell; a Pt wire was used as counter electrode, Ag/AgCl (3 M KCl) as reference, and the photocatalyst (1 cm^2 geometric area) as working electrode. The electrolyte used was an aqueous solution of Na_2SO_4 (0.5 M); experiments using Na_2SO_4 (0.5 M) in ethanol aqueous solution (5 % v/v) were also carried out. For the preparation of the working electrode, 10 mg of sample were dispersed by ultrasonication in deionized water (1 mL) with Nafion (0.1 mL). The dispersion was deposited onto a fluorine-doped tin oxide glass and heated at 120°C for 1 h to evaporate the solvent. EIS measurements were carried out at open circuit conditions in the frequency range of 0.1 Hz to 100 kHz. Transient photocurrent values were recorded at 0 and 0.6 V. The measurements under illumination were carried out using a 150 W AM 1.5G solar simulator (Solar Light Co., 16S-300-002 v 4.0) operating at 1 Sun (100 mW cm^{-2}).

2.3. Photocatalytic performance determination

The photocatalytic performance was evaluated at atmospheric

pressure in both gas and liquid phase using ethanol_(aq). In the first case, a tubular glass photoreactor with a capacity of 40 mL, equipped with a UV light source housing four LEDs emitting at $\lambda = 365 \pm 5$ nm (SACOPA, S. A.U.), was used [32]. The gaseous 9/1 (mol/mol) water/ethanol mixture used was prepared flowing Ar (20 mL min^{-1}) through a liquid water/ethanol solution. 2.0 mg of each prepared photocatalyst was dispersed in absolute ethanol, then drop-casted onto cellulose paper (2.54 cm^2) and dried at 50°C for 1 h. The impregnated paper was positioned between the two sections of the glass photoreactor and the flow containing the gaseous water/ethanol mixture was introduced. An irradiance of $65 \pm 0.5 \text{ mW cm}^{-2}$ was measured on the sample surface using a UVA radiation monitor (Solar Light Co.). Gaseous products were periodically monitored online using a gas micro-chromatograph (Agilent 490). Under these conditions, it was possible to determine the apparent quantum yield (AQY), which was calculated from the amount of generated H_2 and incident photons (see [Supplementary Material](#)).

When the photocatalytic performance was studied in liquid phase, about 300 mg of catalyst were suspended in 250 mL of an ethanol/water (25 % v/v) solution and, under a continuous Ar flow (20 mL min^{-1}) and agitation, irradiated for 4 h at 25°C using a broad-spectrum commercial Hg lamp (ACE-Hanovia, maximum power at $\lambda = 366 \text{ nm}$, [Fig. S1](#)), which was immersed in the photoreactor vessel as previously reported [6]. The outlet flow was periodically analyzed online with a gas micro-chromatograph (Varian CP-4900) and each data point taken at least

twice. In this case, in order to determine the stability of the photocatalysts, after the initial photocatalytic test (4 h), the lamp was switched off and the suspension kept under Ar flow for 16 h. Then, three new 1 h tests were carried out with dark periods between them of 15 min.

2.4. In situ IR study

IR spectra were collected using a Bruker Equinox 55 spectrometer. The samples were pressed in self-supported thin pellets, suitable for transmission experiments, and placed in quartz cells with KBr windows designed to carry out spectroscopic measurements in a controlled atmosphere. The resulting IR spectra were normalized to the pellet 'optical density' (mg/cm^2), in order to make differences in absorbance independent from differences in the thickness of the pellets. For *in situ* UV-Vis irradiation during the IR experiments, a Newport 500 W Hg(Xe) arc lamp was employed with a water filter to eliminate the infrared portion of the spectrum. The UV-Vis radiation was focused on the sample pellet using an aspherical fiber bundle focusing assembly and a large core liquid light guide [33,34].

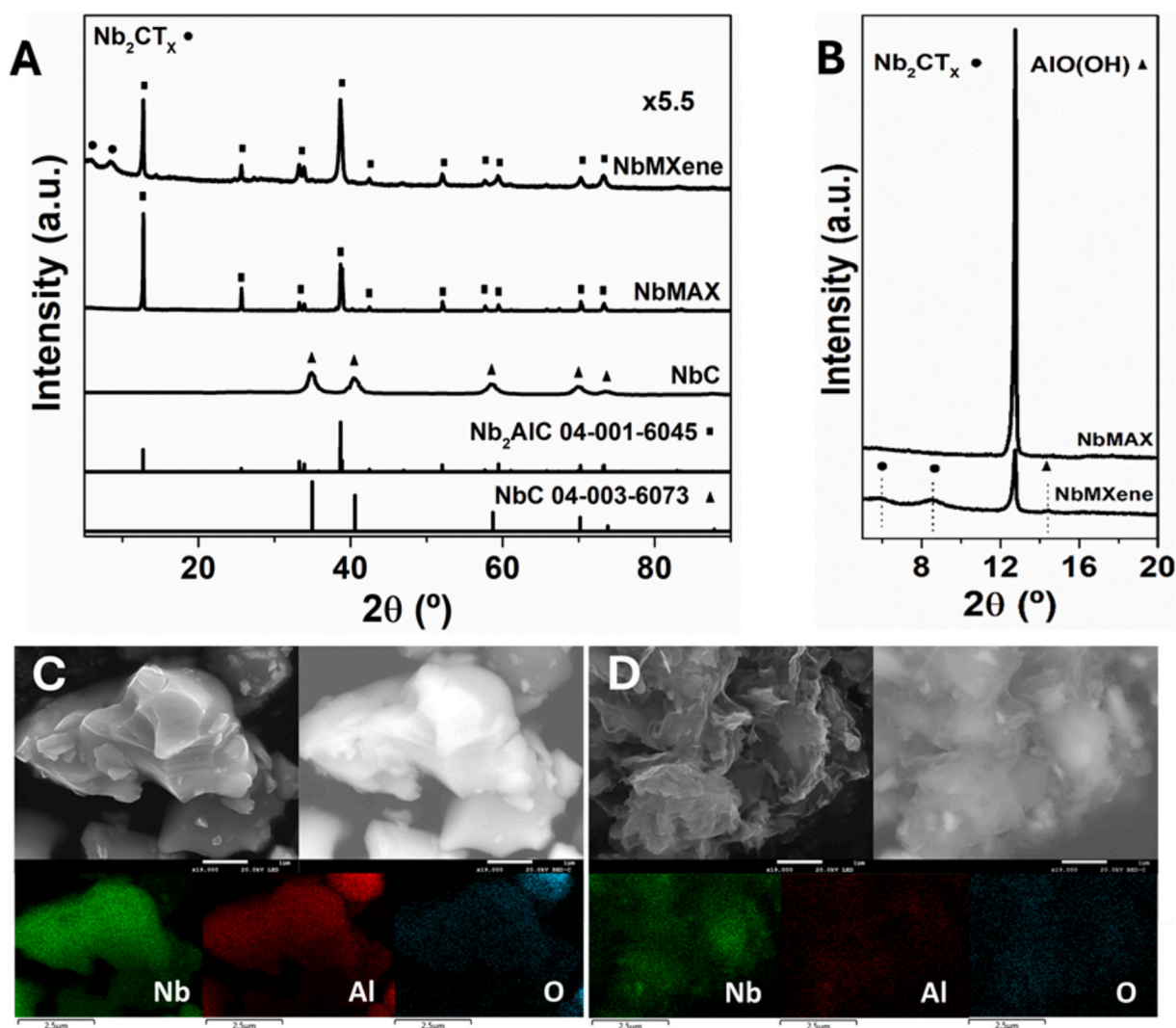


Fig. 1. Characterization of NbC, commercial NbMAX, and NbMXene used in the composite fabrication. A) XRD patterns; B) Magnification of the XRD patterns of commercial NbMAX and derived NbMXene in the $5\text{--}20^\circ$ 2θ range; C) SEM images and EDS mapping of NbMAX and D) SEM images and EDS mapping of NbMXene.

3. Results and discussion

3.1. Characterization of NbC, NbMAX and NbMXene co-catalysts

Fig. 1A depicts the XRD patterns of NbC, commercial NbMAX and derived NbMXene used in the preparation of composite photocatalysts. The pattern of synthesized NbC is assigned to cubic NbC (ICDD 04–003–6073). For commercial NbMAX, hexagonal Nb₂AlC (ICDD 04–001–6045) can be recognized as the dominant phase; however, the presence of minor amounts of other MAX phases, such as Nb₄AlC₃ (ICDD 04–015–4176) and Nb₃Al₂C (ICDD 04–005–3701), cannot be ruled out (see peaks with very low intensity at $2\theta = 7.3, 14.7, 17.7$ and 21.7° in Fig. S2). The presence of a small amount of Nb₄AlC₃ has been previously reported also for other commercial Nb₂AlC [35].

As stated before, NbMXene was prepared for the first time in this work by hydrothermal treatment of commercial Nb₂AlC with NH₃(aq). The removal of aluminum from the MAX phases induces an expansion in the 002 interplanar distance resulting in a shift of the diffraction peak to lower 2θ value than that of the parent MAX phases. Moreover, the presence of interlaminar species can increase the 002 interplanar distance, as previously reported for Ti₃C₂T_x MXene with interlaminar Na⁺ [23]. The corresponding XRD pattern of the synthesized material (Fig. 1A, 1B), shows two wide peaks centered at low diffraction angles, $2\theta = 8.56^\circ$ and 5.98° , which could be reasonably attributed to the (002) crystallographic plane of MXene phases, i.e. Nb₂CT_x. In our case, the presence of nitrogen containing species, probably NH₄⁺ groups, as determined from XPS and IR analysis (Figs. S3 and S4) could lead to Nb₂CT_x with a higher 002 interplanar distance. The observation of two diffraction peaks at low angle is attributed to the coexistence of Nb₂CT_x with different 002 interplanar distances due to the presence of interlaminar NH₄⁺. Besides the peaks associated with the presence of MXene phases, the XRD pattern of NbMXene also shows characteristic peaks of Nb₂AlC, with a much lower intensity than those in the pattern of the NbMAX phase (Fig. 1B). This observation suggests the coexistence of residual Nb₂AlC and randomly stacked MXene layers [36]. The presence of heterojunctions NbMAX/NbMXene could produce an easier electron transfer having a positive effect in the photocatalytic hydrogen production, as has been demonstrated for the 3D WC-Mo₂C system in TiO₂-based photocatalysts [37]. Moreover, the presence of AlO(OH) cannot be ruled out, owing to the appearance of a signal with very low intensity at 14.41° , which can be assigned to the most intense (020) AlO(OH) peak (Fig. 1B).

SEM analysis of NbMAX and NbMXene, used as co-catalysts, brought to light that the hydrothermal treatment of the NbMAX phase produced a strong change in its morphology (Fig. 1C and 1D). The NbMXene showed a discernibly more disordered structure, presenting agglomerations of smaller lamellar structures. Notably, the surface exhibited pronounced roughness, suggesting significant alterations induced by the treatment. The EDS mapping of NbMAX indicated a homogeneous distribution of Nb associated with Al along the sample. However, in some areas, Al seemed predominantly associated with O, likely due to the presence of residual aluminum oxide species (Fig. 1C); the O 1s XPS spectrum (Fig. S5) showed two components centered at 530.3 and 531.8 eV, which could be related to O²⁻ and OH⁻ of the residual aluminum species [38]. When the EDS mapping of NbMXene (Fig. 1D) is compared to that of pristine NbMAX, a significant decrease in the signals coming from Al and a homogeneous distribution of Nb and O is visible, in line with the presence of NbMXene (i.e. Nb₂CT_x, Nb₄CT_x; T = O, OH). The O 1s XPS spectrum (Fig. S5) is now dominated by a main component centered at 530.6 eV, probably related to the presence of Nb-C-O_x, the minor component at 531.9 eV could be related to C-Nb-(OH)_x [39]. However, residual oxo/hydroxo aluminum species could also contribute to the NbMXene O 1s spectrum. From EDS quantification a (Nb/Al)_{EDS} atomic ratio of 1.9 and 6.4 for pristine NbMAX and derived NbMXene was determined, respectively (Table S1). The removal of Al from NbMAX after the hydrothermal treatment was also confirmed by XPS

(Fig. S5), being the (Nb/Al)_{XPS} atomic ratio 1.2 and 12.0 for the NbMAX and the corresponding NbMXene, respectively.

The TEM-HRTEM characterization of synthesized NbMXene (Fig. 2) showed a multilayered laminar structure with interplanar distance of 10.94 Å, assigned to the (002) plane of the Nb₂CT_x MXene phase. However, residual Nb₂AlC MAX and bohemite were also identified (Fig. S6). All these findings are in agreement with the above discussed XRD results (Fig. 1B).

3.2. Characterization of composite photocatalysts

As stated in the experimental section, composites were fabricated from Nb carbide-based materials and anatase TiO₂, using ultrasounds. The Nb content (Table 1) was similar in all the photocatalysts (2.8–2.9 wt%). The BET surface area values were in the 8–18 m² g⁻¹ range, being the lowest and the highest those of pristine anatase and NbMXene/TiO₂, respectively.

The XRD patterns of the composites showed intense characteristic peaks of anatase TiO₂ (Fig. S7) but diffraction peaks due to the co-catalysts (NbC, Nb₂C MXene and Nb₂AlC MAX) were not observed; this is probably related with the small amount of carbide-derived materials incorporated (Table 1). Raman analysis of the composites also indicated that, during their fabrication, TiO₂ remained as anatase phase and no other species were detected by this technique (Fig. S8).

From the UV–Vis DRS measures, using the Kubelka-Munk formalism and the Tauc plots (Fig. S9), the band gap energies (E_g) were determined according to a reported method [40]. The E_g values are shown in Table 1, no significant variations in the E_g values of nanocomposites with respect to that of anatase are noted.

All composites were also analyzed by TEM-HRTEM (Fig. 3). As expected, small particles of NbC on TiO₂ were detected for NbC/TiO₂ composite (Fig. 3A), however, Nb₂O₅ was also found in some areas (Fig. S10). As expected, the presence of Nb₂AlC particles was confirmed in NbMAX/TiO₂ (Fig. 3B).

Fig. 3C shows stacked laminar structures of Nb₂CT_x in NbMXene/TiO₂, interplanar distances of 8.9 and 9.1 Å, assigned to (002) planes, were determined. The slight decrease in the (002) interplanar distances, compared to those determined for synthesized Nb₂CT_x (Fig. 2), could be related to the removal of the interlaminar species during the composite preparation process.

XPS analysis of as prepared composites revealed besides the presence of Nb₂O₅, that of Nb⁴⁺ and other species containing Nb-C bonds (Fig. S11) [41–43]. The Ti 2p BE characteristic of TiO₂ (Ti 2p_{3/2} BE = 458.5–458.7 eV) was found in all cases. The surface Nb/Ti atomic ratio determined for NbMXene/TiO₂ was much higher than those of NbMAX/TiO₂ and NbC/TiO₂ (Table 1).

3.3. Photoelectrochemical properties and photocatalytic hydrogen production

Photoluminescence (PL) spectroscopy was employed to assess the dynamics of the charge carriers, since the PL spectral features are determined by the photoinduced charge recombination, and can be related to the photoactivity of the material [44,45].

In all cases, a broad PL band centered at about 580 nm is present (Fig. 4A), which can be ascribed to the presence of a high density of defect sites in anatase [46]. However, the photocatalysts showed PL bands with different intensities (Fig. 4A): the highest and the lowest intensity were found for pristine TiO₂ and NbMXene/TiO₂, respectively (being the order: TiO₂ > NbMAX/TiO₂ > NbC/TiO₂ > NbMXene/TiO₂). A lower intensity of the PL band indicates a lower e⁻/h⁺ recombination rate [45] and, thus, an easier release of the generated e⁻ able to reduce the H⁺, which can be associated with the photoactivity in H₂ production [5,47]. Electrochemical impedance spectroscopy (EIS) was performed both under simulated solar irradiation and in dark conditions (Figs. 4B and S12). The arc radius within the corresponding Nyquist plots can be

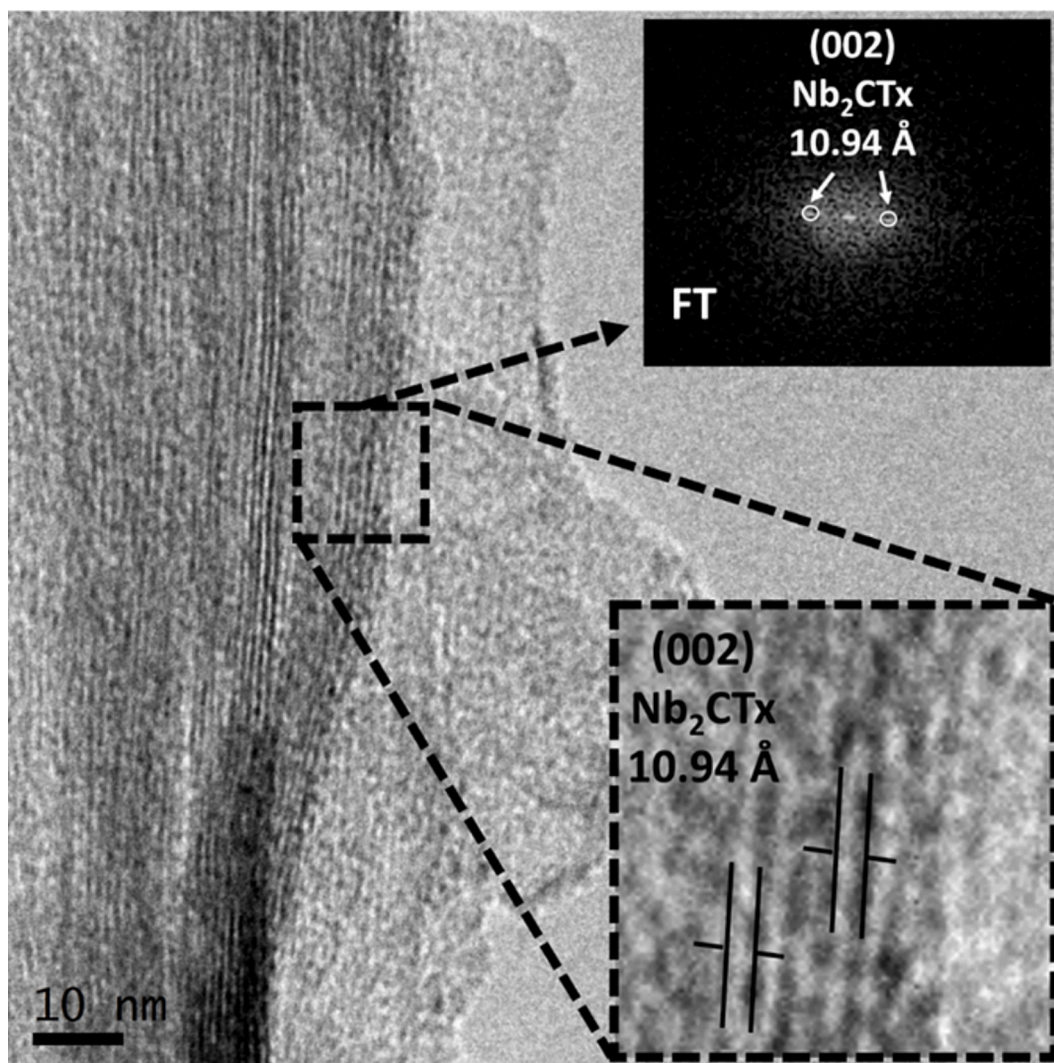


Fig. 2. TEM-HRTEM images of synthesized NbMXene used in the composite fabrication. In the insets Fourier transforms and interplanar distances are reported.

Table 1

BET surface area, niobium content, band gap energy values (E_g) and Nb/Ti atomic ratio determined by XPS of anatase TiO_2 and composites.

Sample	S_{BET} (m^2/g)	Nb (wt %)	E_g (eV)	(Nb/Ti) _{XPS}
TiO_2	8	—	3.32	—
NbC/ TiO_2	13	2.86	3.31	0.004
NbMAX/ TiO_2	9	2.90	3.31	0.003
NbMXene/ TiO_2	18	2.79	3.31	0.018

related to the resistance encountered in transferring the photogenerated electrons, thus a smaller arc radius denotes lower resistance. All photocatalysts exhibited smaller arc radii under irradiation (Fig. 4B) than under dark conditions (Fig. S12). Moreover, all the composites showed lower arc radius than TiO_2 under both conditions, this is particularly evident for the NbMXene/ TiO_2 sample. Under the experimental conditions used, no diffusion effects are expected; the EIS curves can be fitted to the Randle model and the equivalent circuit calculated (Fig. S13). NbMXene showed the lowest resistance to the charge transfer and TiO_2 the highest. In all cases the resistance decreased under illumination (Fig. S13). A similar behavior was determined when ethanol was present in the electrolyte solution (Fig. S14). To complete the photoelectrochemical characterization, the transient photocurrent response of the materials was investigated using on/off pulses of simulated solar irradiation. Moreover, to determine how the presence of ethanol can

influence the transient photocurrent response for the different materials, the measures were carried out also in the presence of a 5 % v/v ethanol solution; a higher photocurrent value indicates a higher photoelectron yield under the irradiation used. Fig. 5 shows the photocurrent responses measured at open circuit using as electrolyte the solution containing ethanol (Fig. 5 blue curves) or not (Fig. 5 black curves). For the composites, the presence of ethanol produces an increase in the photocurrent response, meanwhile this effect is not seen for pristine anatase. When Nb carbide-based materials are present, the presence of ethanol could decrease the electron-hole recombination producing an increase of the photocurrent response. Moreover, a contribution of the called “Current Doubling” effect cannot be ruled out [48]. The presence of carbide-based materials is related to the improvement of the kinetics of ethanol oxidation compared to that of water. This was further confirmed when the measures were carried out at a higher potential, to favor the oxidation process. A higher increase in the photocurrent was determined at 0.6 V (Fig. S15). The interaction of ethanol with the photocatalyst could form the α -hydroxyethyl radical, which could evolve into acetaldehyde and provide one electron to the conduction band, increasing the photocurrent response [48].

As stated in the experimental section, the photocatalytic performance of composites was evaluated at atmospheric pressure, in both gas and liquid phases, using ethanol_(aq) solutions. Fig. 6 shows the H_2 photoproduction determined from the different tests. The rate of H_2 production from the test carried out in gas phase is shown in Fig. 6A. In

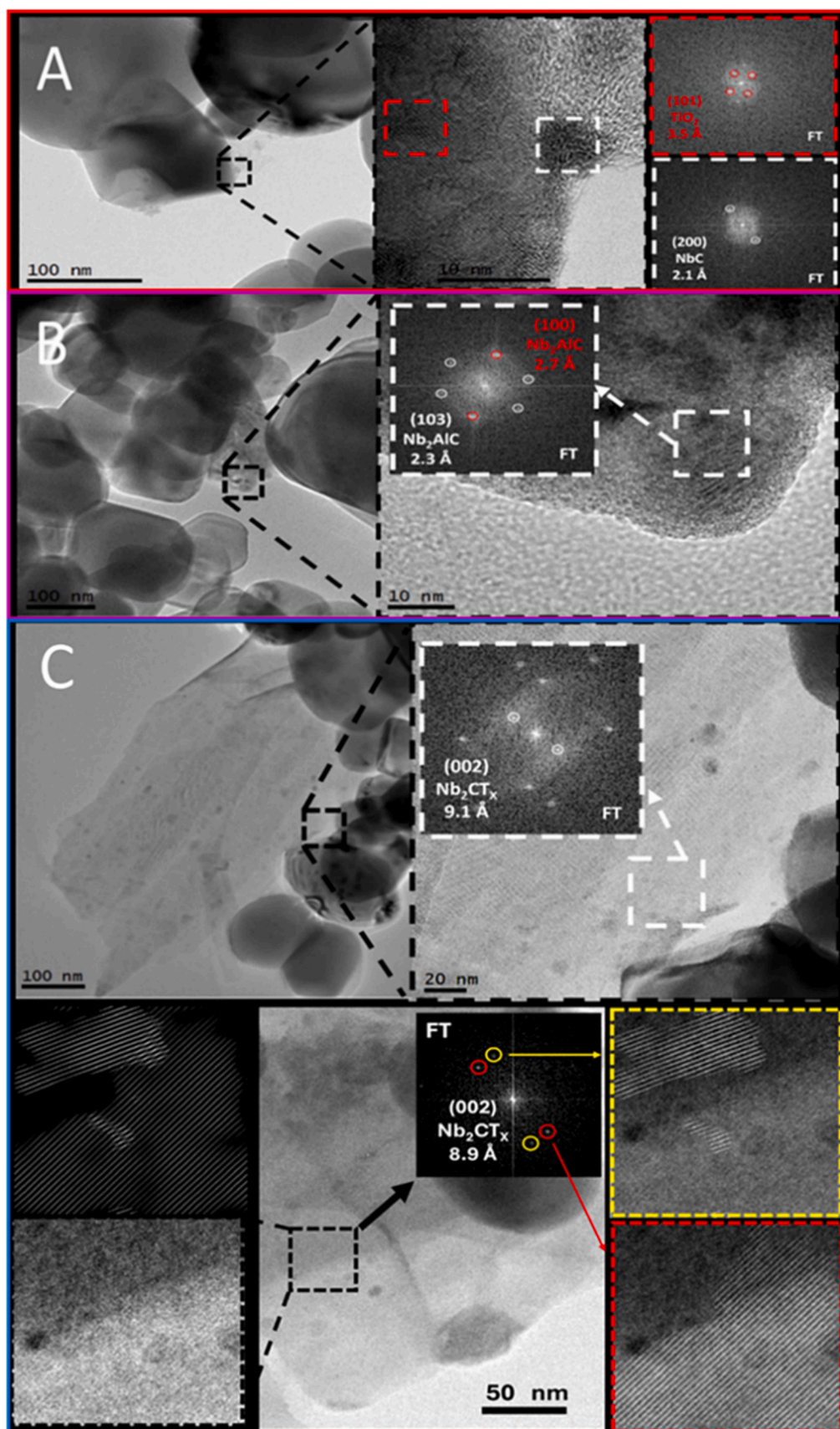


Fig. 3. TEM-HRTEM images of different zones of NbC/TiO₂ (A), NbMAX/TiO₂ (B) and NbMXene/TiO₂ (C). In the insets the Fourier transforms with interplanar distances are reported. For NbMXene/TiO₂ (C), inverse Fourier Transform of spots (bottom right) shows the different plane orientation of superposed MXene sheets.

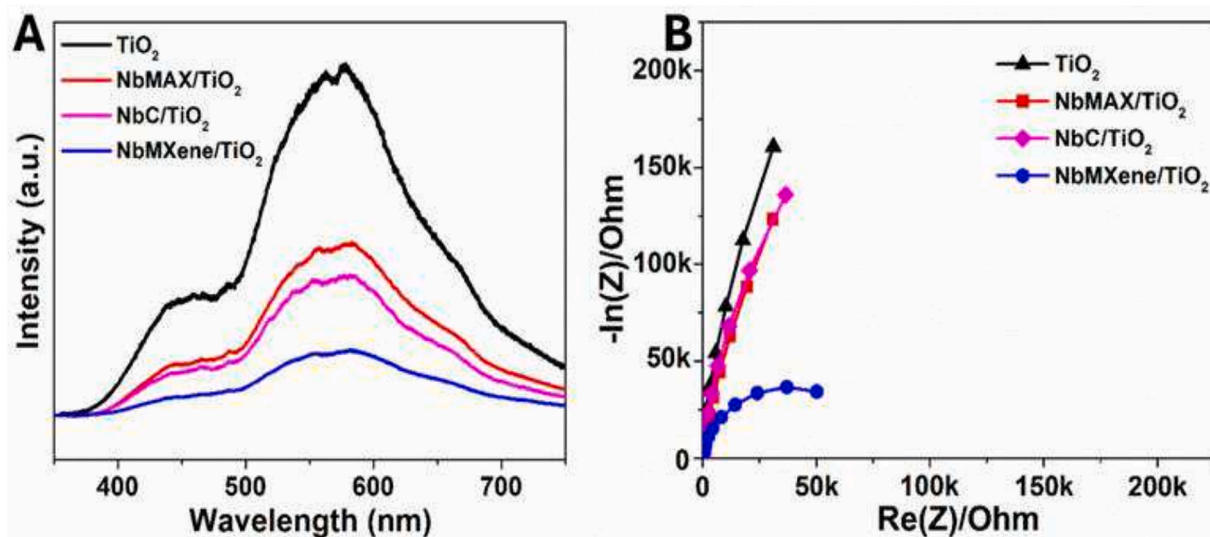


Fig. 4. A) Photoluminescence spectra; B) EIS Nyquist plots under simulated solar irradiation for the different photocatalysts in the absence of ethanol.

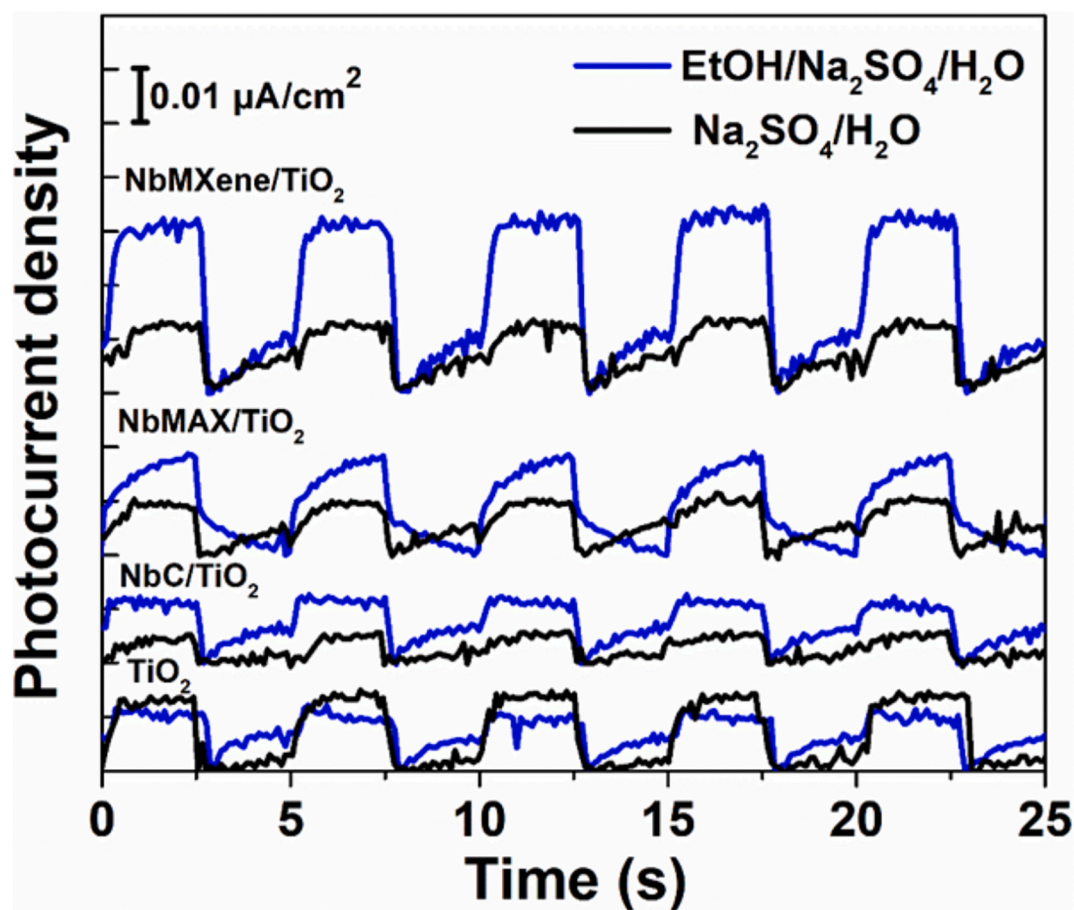
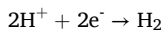
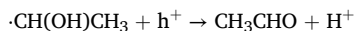
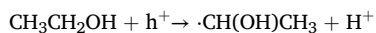


Fig. 5. Transient photocurrent response of the nanocomposites using on/off pulses of simulated solar irradiation at open circuit. Blue and black curves correspond to the measurements carried out in the presence or in the absence of ethanol (5 % v/v), respectively.

all cases, the stable rate of H_2 production during the test (1 h) is remarkable. The exclusive production of hydrogen and acetaldehyde in equimolar amounts was found and no CO_2 production was detected.

Once the photogenerated e^-/h^+ pairs reach the surface, H_2 and acetaldehyde can be formed following:



The presence of Nb carbide-based materials onto anatase TiO_2 , increased in all cases the H_2 production. This is related with the role of

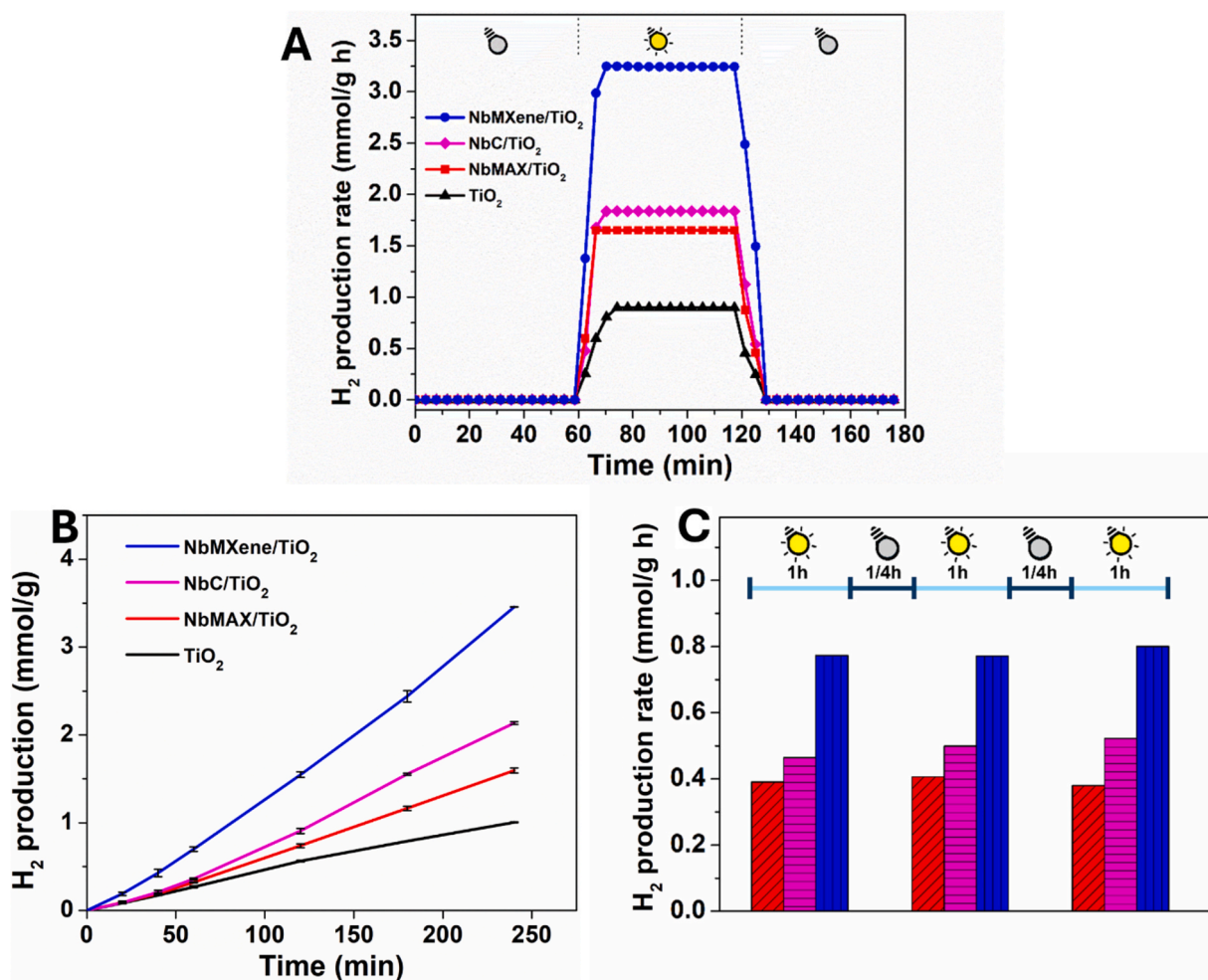


Fig. 6. H₂ photoproduction from ethanol aqueous solutions using Nb carbide-based/TiO₂ composites in gas (A) and liquid phase (B and C). A) H₂ production rate using ethanol/water 1/9 mol/mol in gas phase; B) total amount of H₂ produced during the first run (4 h) in liquid phase using 25 % (v/v) ethanol aqueous solution; C) after B) and 16 h in the dark, stability tests (red bars: NbMAX/TiO₂, pink bars: NbC/TiO₂, blue bars: NbMXene/TiO₂).

co-catalysts providing a site for trapping e⁻, which will be used in the H⁺ reduction. From the values of H₂ production, the apparent quantum yield was determined (AQY, see [Supplementary Material](#) for further details): NbMXene/TiO₂ (AQY = 0.76 %) > NbC/TiO₂ (AQY = 0.43 %) > NbMAX/TiO₂ (AQY = 0.39 %) > TiO₂ (AQY = 0.21 %).

A similar order was also found for the amount of H₂ produced when the photocatalytic tests were carried out in liquid phase (Fig. 6B). NbMXene/TiO₂ produced the highest H₂ amount: 3.46 mmol/g after 4 h of reaction. As stated above, NbMXene/TiO₂ exhibited the lowest electron transfer resistance, the lowest recombination rate of the photo-generated charges and the highest photocurrent in the presence of ethanol. The intimate interface between TiO₂ and the NbMXene, produces a very efficient transfer of the photogenerated electrons from the TiO₂ conduction band to the co-catalyst. This favors the supply of electrons to the NbMXene surface, where preferentially the H⁺ reduction will take place. Moreover, the outstanding electron conductivity of NbMXene certainly contributes to the photocatalytic behavior of NbMXene/TiO₂ [49].

Finally, after the 4 h photocatalytic test and a dark period, the stability of catalysts was determined following up to three light on/light off cycles (Fig. 6C). The stability tests pointed out a constant performance of the nanocomposites; only slight variations in the values of H₂ production (below 5 %) were found (Fig. 6C). Moreover, the reproducibility of the photocatalytic behavior of the prepared nanocomposites was proved in a new separate test under other conditions of light on/light off cycles (Figs. S16 and S17).

3.4. In situ IR study

To get deeper insights into the surface processes occurring during the photocatalytic reaction, we performed an *in situ* IR study. As first step, we investigated the interaction of the different composites with ethanol (Fig. 7), which is employed as hole scavenger, having a key role in the reaction. Comparing the intensity of the spectral features in the different samples, we can readily notice that pristine anatase TiO₂ can adsorb approximately 10 times more ethanol than the composites. Concerning the adsorption structures, we can identify signals that have been assigned to ethoxide species, as the ν(CCO) vibrations at 1070 cm⁻¹ [50,51]. At the same time, we can find also bands that are considered a fingerprint of molecular ethanol, like the δ(OH) at 1270 cm⁻¹ [50,51]. To try to better understand the amount of molecular and deprotonated ethanol present in the different samples, we focus on the ν(CH) bands in the 3000–2800 cm⁻¹ spectral region. Previous studies assigned the signals at ca. 2970, 2930 and 2870 cm⁻¹ to molecular ethanol and the peaks at 2900 and 2850 cm⁻¹ to ethoxide [52].

From the analysis of these bands, we can conclude that NbMAX/TiO₂ and NbMXene/TiO₂ show a higher fraction of dissociated ethanol.

Subsequently, to mimic the conditions employed in the photocatalytic experiments, water vapor was dosed on the sample with pre-adsorbed ethanol. As visible in Fig. 8, in all samples the presence of a multilayer of molecular water is testified by the appearance of a band associated to the δ(H₂O) mode at ca. 1640 cm⁻¹ [53].

Considering the intensity of the water bending signal and that of the

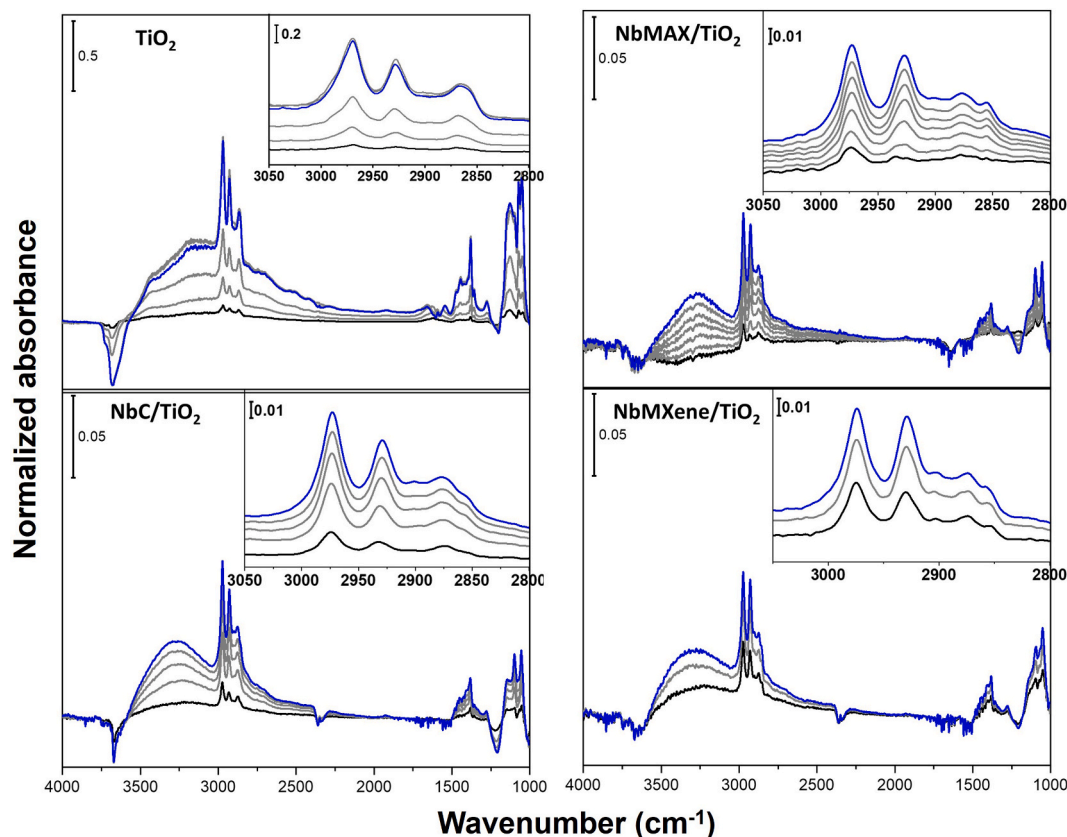


Fig. 7. IR spectra of ethanol adsorption at increasing pressures (up to 5 mbar, blue curve) for the photocatalysts previously outgassed at 120 °C for 1 h. In the inset a magnification of the $\nu(\text{CH})$ spectral region is reported. The spectrum of the activated material has been subtracted from all spectra.

$\nu(\text{OH})$ band in the 3700–3000 cm^{-1} spectral region, we can highlight that the hydrophilicity of the material is significantly reduced upon functionalization with the co-catalyst, in agreement with the results obtained for ethanol adsorption. Then, the spectra acquired under UV–Vis irradiation at increasing times show a slight decrease in the intensity of the ethanol signals, ascribed to its photooxidation while acting as an electron donor to produce H_2 . In parallel, we can notice a modification of the sample scattering profiles due to the absorption of IR radiation by the UV-generated free conduction band electrons [54,55]. Interestingly, the extent of the absorbance increase, associated with the presence of charge carriers in the TiO_2 conduction band, follows the order: $\text{TiO}_2 > \text{NbMAX}/\text{TiO}_2 > \text{NbC}/\text{TiO}_2 > \text{NbMXene}/\text{TiO}_2$, which reflects the trend observed in the photocatalytic activity measurements and intensity of PL bands. These findings suggest that in $\text{NbMXene}/\text{TiO}_2$ we have a very efficient transfer of the photogenerated electrons from the TiO_2 conduction band to the MXene phase, with a consequent limited increase in IR absorbance and efficient H_2 production.

4. Conclusions

Different Nb based-carbides on TiO_2 are compared in the photocatalytic H_2 production from ethanol_(aq), both in gas and in liquid phase. A new hydrothermal method, using $\text{NH}_3(\text{aq})$, was employed to extract Al from the Nb_2AlC MAX phase, rendering multilayered Nb_2CT_x ($T = \text{O}, \text{OH}$) MXene. NbC/TiO_2 , $\text{NbMAX}/\text{TiO}_2$ and $\text{NbMXene}/\text{TiO}_2$ composites were successfully prepared, from commercial anatase TiO_2 and the corresponding co-catalyst, using an ultrasound-assisted method. The textural and structural characteristics of pristine TiO_2 were kept in the composites. The photocatalytic performance of the composites can be related to their photoelectrochemical characteristics, which depended on the co-catalyst used. In both, gas and liquid phase, the order of H_2 photoproduction was $\text{NbMXene}/\text{TiO}_2 > \text{NbC}/\text{TiO}_2 > \text{NbMAX}/\text{TiO}_2 >$

TiO_2 . Notably, $\text{NbMXene}/\text{TiO}_2$ produced about 3.2 $\text{mmol g}^{-1} \text{h}^{-1}$ in gas phase; the only products found were acetaldehyde and H_2 in equimolar amounts. Indeed, $\text{NbMXene}/\text{TiO}_2$, which exhibited the best photocatalytic performance in the H_2 production, also showed the minimum electron transfer resistance and the highest photocurrent response in the presence of ethanol. *In situ* IR experiments evidenced the formation of dissociated ethanol species and the effective role of co-catalysts increasing the lifetime of the electron-hole couples, which follows the order $\text{NbMXene}/\text{TiO}_2 > \text{NbC}/\text{TiO}_2 > \text{NbMAX}/\text{TiO}_2 > \text{TiO}_2$. The close interaction between TiO_2 and NbMXene and the remarkable electronic conductivity of NbMXene , certainly lead to the efficient transfer of the photogenerated electrons from the TiO_2 conduction band to the NbMXene . This transfer is more effective in the presence of ethanol, which favors the oxidation process, producing acetaldehyde. All composites show stable photocatalytic behavior and can be easily re-utilized in the conditions used in this study.

CRediT authorship contribution statement

Adrià Sánchez: Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Guillermo Escolano-Casado:** Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Margarita Bania:** Methodology, Investigation, Formal analysis, Data curation. **Matthijs Koning:** Methodology, Investigation, Formal analysis, Data curation. **Jaroslav Serafin:** Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Pilar Ramírez de la Piscina:** Conceptualization, Formal analysis, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. **Lorenzo Mino:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Narcis Homs:** Writing – review & editing, Writing – original draft, Validation,

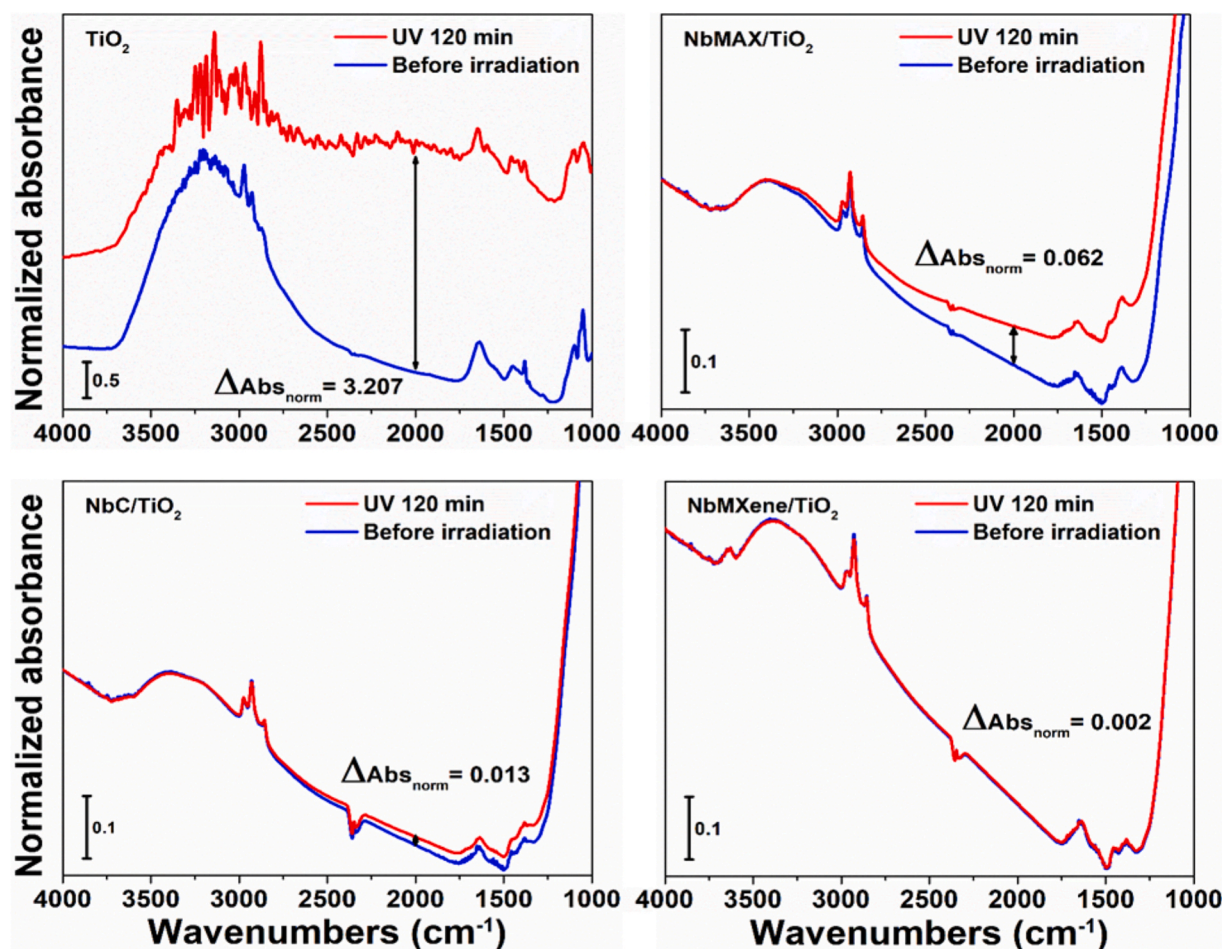


Fig. 8. IR spectra of the photocatalysts upon adsorption of ethanol and water in dark conditions (blue curves) and after 120 min of irradiation (red curves). The increase in normalized absorbance after irradiation at 2000 cm^{-1} is indicated.

Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2025.163797>.

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