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2 **Mo₂CT_x MXene supported nickel-iron alloy: an efficient and stable**
3 **heterostructure to boost oxygen evolution reaction**

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12
13 **Abstract.** A polyol-assisted solvothermal route is used to synthesize Ni_xFe_y nanoalloys
14 supported on a highly electron conductive 2D transition metal Mo₂CT_x MXene. Structural,
15 morphological and chemical characteristics of the materials are determined using several
16 physicochemical techniques. The MXene support allows not only the formation of a
17 nanostructured metallic Ni_xFe_y nanoalloys, but also favors the interfacial charge transfer for the
18 OER. The Ni_xFe_y@Mo₂CT_x material with a Ni/Fe ratio of 2.66 leads to the outstanding activity
19 for the OER with an amazingly low Tafel slope value of 34 mV dec⁻¹ and a current density of 10
20 mA.cm⁻² at a potential of only 1.50 V vs. RHE. *In situ* Raman experiments show that β-NiOOH
21 formed by oxidation of the nanoalloys under positive scan, likely containing a very small amount
22 of Fe, is the active phase for the OER. This material exhibits also an excellent stability over 168
23 h in a 5 M KOH electrolyte. TEM-EELS analyses after 100 voltammetric cycles between 0.2 to

24 1.55 V vs. RHE evidence for the first time that the MXene support is not fully oxidized in the
25 first cycle. Also, oxyhydroxide layer formed in the OER potential region at the surface of the
26 Ni_xFe_y nanoparticles can be reversibly reduced.

27 **Keywords.** MXene, nickel-iron alloy, molybdenum carbide, oxygen evolution reaction, polyol
28 synthesis route

29

30 1. Introduction

31 The oxygen evolution reaction (OER) plays a key role for the emergence of energy storage and
32 conversion devices such as rechargeable metal-air batteries and electrolyzers required for the
33 implementation of the future energy grid [1-2]. However, the OER involves a complex
34 mechanism with several proton-coupled electron transfer processes and suffers from a sluggish
35 kinetics [3-5]. The use of electrocatalysts can strongly reduce the reaction activation energy and
36 enhance reaction kinetics, prerequisites to allow the future large-scale production of green H_2
37 and the design of high energy efficiency rechargeable metal-air batteries. The design of efficient
38 catalysts exhibiting a high stability under harsh working conditions encountered in real systems
39 is thus a current major stumbling block.

40 In alkaline medium, 3d transition metals such as Mn, Ni, Co and Fe are both OER-active
41 materials and thermodynamically stable in the OER potential range. This makes them attractive
42 candidates for the design of low-cost, abundant and noble metal-free catalysts. A wide range of
43 materials combining these elements under various forms have been reported in recent years such
44 as (hydr)oxides [6-8], chalcogenides [9], phosphides [10], nitrides [11], sulfides [12] and borides
45 [13]. Among all possibilities, catalysts combining iron and nickel elements are the most
46 promising ones [14-17].

47 Several strategies were devised to improve the OER activity of Ni and Fe based
48 electrocatalysts, aiming at exposing more active sites to the electrolyte [18], optimizing the Ni/Fe
49 composition and synthesizing materials with structural defects to regulate the electronic structure
50 [19]. The amazing OER activity of these materials has been ascribed to different phenomena and
51 still remain under debate [20-23]. The understanding of both the dynamic reconstruction and the
52 evolution of the electrode/electrolyte interface induced by variations of the electrode potential
53 must be completed.

54 These materials are often deposited onto various substrates to improve their dispersion and to
55 avoid aggregation processes under reaction conditions. The strong coupling with conductive
56 materials such as carbon-based substrates [24-28] promotes fast charge transfer at the engineered
57 heterointerface [29] and modulates the local electronic structure of active sites [25, 30].
58 Nevertheless, the stability of such heterostructures at potentials required for the OER, *i.e.*, higher
59 than 1.23 V *vs.* the reversible hydrogen electrode (RHE), remains questionable [31], the
60 thermodynamic potential of the CO₂/C redox couple being 0.205 V *vs.* RHE.

61 Two dimensional carbides called MXene have recently attracted much attention as substrates
62 for the deposition of OER active phases [32-35]. MXene sheets, with a general formula of
63 $M_{n+1}X_nT_x$, are obtained from MAX phases (formula : $M_{n+1}AX_n$, with M a transition metal, A
64 generally an element from the 13th or 14th column of the periodic table and X corresponds to
65 carbon and/or nitrogen) by exfoliation of the A element and then delamination [36-40]. The
66 delaminated MXenes present high specific surface areas and electronic conductivity, as well as
67 hydrophilic properties. Terminal groups (T of $M_{n+1}X_nT_x$, generally -O, -OH and/or -F, formed
68 during the exfoliation process) at the surface act as anchoring sites for the active phase, and
69 allow a high chemical versatility to tune the heterointerface interaction and the local electronic

70 structure of the MXene/active phase [41], making them relevant as supports for active
71 electrocatalysts. However, irreversible oxidation of MXenes occurs at high potential [42, 43],
72 although the oxidation depth remains undetermined. Numerous studies were reported on $Ti_3C_2T_x$
73 [44-48], $Mo_2TiC_2T_x$ [49] and V_2CT_x [50] substrates for Ni and Fe-based active phases. **But, Ti,**
74 **corresponding to the metallic element most often encountered in MXenes, has recently been**
75 **included in the list of critical raw materials and has therefore to be avoided in catalyst support**
76 **formulation. Molybdenum is a non-critical metal and Mo_2CT_x MXenes could be good**
77 **alternatives to Ti containing MXenes.**

78 Herein, Ni and/or Fe based active phases have been heterogeneously nucleated and grown onto
79 a Mo_2CT_x MXene thanks to a simple polyol-assisted solvothermal method. The use of numerous
80 physicochemical techniques enabled the comprehensive characterization of the morphology, the
81 structure and the composition of the as-synthesized materials. It was first demonstrated that the
82 chemical nature of nickel-iron crystalline phases was influenced by the surface chemistry of the
83 MXene, nanoalloys being successfully synthesized only in the presence of the 2D substrate. The
84 OER activity of NiFe@ Mo_2CT_x materials with different Ni/Fe ratios was further determined in
85 alkaline medium. The most efficient heterostructured catalyst led to a particularly high activity:
86 an electrode potential of only 1.5 V vs. RHE was required to drive a current density of 10 mA
87 cm^{-2} . *In situ* characterization and characterization of the aged materials (after several potential
88 cycling in the OER potential region) were also performed to get insight on the structural
89 evolution of the composite catalysts.

90

91 **2. Experimental section**

92 *2.1 syntheses of materials*

93 The synthesis of $\text{Mo}_2\text{Ga}_2\text{C}$ (MAX-like phase) is performed as described by Benchakar et al.
94 [51]. Gallium is mixed with $\alpha\text{-Mo}_2\text{C}$ powder (50 μm , 99.5%, Alfa Aesar) in a 1:8 molar ratio.
95 The mixture is crushed in a mortar to obtain a homogeneous paste. The paste is transferred into a
96 vacuum glass tube and thermally treated under argon flow at 850 $^\circ\text{C}$ (temperature ramp of 5
97 $^\circ\text{C}/\text{min}$) for 7 days. The powder is recovered and treated with hydrochloric acid (35%,
98 TECHNICAL, VWR) overnight under magnetic stirring to remove the excess of gallium. The
99 powder is washed with ultrapure water (MilliQ[®], Millipore, 18.2 $\text{M}\Omega$ at 20 $^\circ\text{C}$), filtered and
100 dried under air. Finally, the powder is sieved in order to select grain sizes lower than 25 μm .

101 The synthesis of Mo_2CT_x is described elsewhere [51]. Briefly, 1 g of the $\text{Mo}_2\text{Ga}_2\text{C}$ powder is
102 put in 20 mL of a 48% HF solution. The mixture is magnetically stirred before being heated at 60
103 $^\circ\text{C}$ for 196 h. The suspension is then washed with ultrapure water and centrifuged at 3500 rpm
104 (1575 g) in a rotor F-34-6-38 (Eppendorf centrifuge 5804) several times until the pH value of the
105 supernatant solution is close to 5. The resulting powder is mixed with 5 mL of an aqueous
106 solution of tetrabutylammonium hydroxide (1.5 mol L^{-1} TBAOH aqueous solution, ACROS
107 OrganicsTM) to delaminate the MXene. The mixture is vortexed for 2 min and then ultrasonicated
108 under argon for 30 min to insert TBA^+ ions between MXene sheets. The powder is settled down
109 by centrifugation at 3500 rpm for 2 min, the supernatant solution removed and absolute ethanol
110 ($\geq 99.9\%$, CARLO ERBA) added. The latter procedure is repeated 4 times. Ultrapure water is
111 added and the mixture is centrifuged for 30 min at 2500 rpm (804 g) to form a colloidal
112 suspension of Mo_2CT_x MXene sheets. The suspension is then filtered to recover pure MXene
113 sheets. The retentate is finally dried in a desiccator under atmospheric pressure and the obtained
114 MXene film is placed in a tube and stored in a glove box under argon.

115 In a tricol, 200 mg of Mo_2CT_x are dispersed in 5 mL of ultrapure water under sonication for
116 10 min to obtain a colloidal suspension. This mixture is dispersed in 200 mL of anhydrous
117 ethylene glycol (EG, 99.8%, AcroSeal®, ACROS Organics), acting as solvent, before being
118 sonicated for 10 min under argon. Metal precursors (nickel (II) acetate tetrahydrate, $\geq 99.0\%$,
119 Sigma-Aldrich and/or iron (III) acetylacetonate, $\geq 99.9\%$, Sigma-Aldrich) are added to the
120 suspension. The solution is magnetically stirred before adding sodium hydroxide (5 g, powder,
121 97.0%, Sigma-Aldrich). The addition of sodium hydroxide allows the formation of glycolate ions
122 that possess a higher reducing ability than EG [52, 53]. The mixture is then magnetically stirred
123 overnight at room temperature under argon atmosphere and transferred in a Teflon lined
124 autoclave before being heated at 200°C for 3 h under nitrogen flow. The reaction mixture is
125 washed by centrifugation in the presence of ethanol at 9000 rpm for 15 min. The supernatant is
126 removed and the procedure is repeated a second time. A last wash is performed with ultra-pure
127 water. The suspension is filtrated with the addition of 100 mL of ultrapure water. The retentate is
128 placed into a desiccator overnight and stored in a glove box under argon flow. For unsupported
129 materials, the procedure is the same as for supported ones except that the MXene is not added.
130 To determine whether this synthesis route affects the MXene structural properties, the synthesis
131 process was also conducted with MXene without any metallic salts (this material is labelled
132 $\text{Mo}_2\text{CT}_x\text{-ST}$). The synthesis procedure of the composite is summarized in Scheme S1 of the
133 supplementary information.

134 The different supported samples are referred to as A/B-NiFe@ Mo_2CT_x where A and B are
135 defined as: A = wt.% Ni and B = wt.% Fe. The composition of all the materials investigated in
136 this study is given in Table 1.

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Table 1. Nominal weight percent of iron, nickel and Mo₂CT_x in the different investigated samples. The synthesis process was also conducted with MXene without any metallic salts. The sample is labelled Mo₂CT_x-ST.

Label	wt.% Mo ₂ CT _x	wt.% Ni	wt.% Fe
Fe	0	0	100
Ni	0	100	0
FeNi	0	50	50
33/17-NiFe@Mo ₂ CT _x	50	33.3	16.7
25/25-NiFe@Mo ₂ CT _x	50	25	25
17/33-NiFe@Mo ₂ CT _x	50	16.7	33.3
Mo ₂ CT _x -ST	100	0	0

146

147 2.2 Material characterization

148 X-Ray diffraction measurements are performed at room temperature over a 2 θ angular range,
149 from 3° to 70°, with a step interval of 0.066° and an acquisition time of 420 s per step using an
150 EMPYREAN PANalytical diffractometer in Bragg-Brentano configuration, equipped with a
151 copper anode source (Cu_{K α 1} = 0.15406 nm). A reduction in analysis time is achieved by using an
152 ultrafast X-ray detector (X'Celerator) based on RTMS (Real Time Multiple Strip) technology.
153 The diffractograms are processed with the HighScorePlus[®] software.

154 The morphology of synthesized materials is analysed by scanning electron microscopy (SEM)
155 using a MEB-FEG JSM-7009F microscope (JEOL company) equipped with a field emission gun

156 and an energy dispersive X-ray spectrometer (EDX) 6/30 from Brücker for the determination of
157 chemical elements in samples. The EDX analyses are performed with the Esprit 2.1 software.

158 Transmission electron microscopy (TEM) samples are prepared by dispersing the materials in
159 deionized water and dispensing a drop of the suspension on a copper TEM grid covered with a
160 lacy carbon film. TEM analysis including energy filtered selected area electron diffraction (EF-
161 SAED) and electron energy-loss spectroscopy (EELS) are performed using a JEOL 2200-FS
162 microscope operated at 200 kV and equipped with an in-column omega filter. The EELS
163 resolution is around 1.1 eV as determined from the full width at half maximum of the zero-loss
164 peak. The EELS spectra are acquired in image mode using a collection semi-angle of 2.4 mRad.
165 When necessary, spectra are deconvolved from multiple scattering using the Fourier-ratio
166 method.

167 The size and morphology of nanoparticles supported onto Mo_2CT_x MXene are investigated
168 using a transmission electron microscope (JEOL JEM-2001). Size distributions presented in
169 supporting information are obtained by counting 100 isolated nanoparticles using the ImageJ[®]
170 free software.

171 The Mo, Ga, Ni and Fe contents of the different materials are determined by Inductively
172 Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using a PerkinElmer Optima
173 2000DV instrument.

174 *2.4 Raman spectroscopy measurements*

175 Raman spectroscopy is carried out using a HORIBA Jobin Yvon LabRAM HR800 confocal
176 Raman microscope with a CCD detector. Spectra are acquired at room temperature (RT) using
177 an excitation wavelength of 632.8 nm, supplied by an internal He-Ne laser. The power delivered

178 is less than 1 mW. An 1800 grooves mm^{-1} grating is used resulting a spectral resolution of 0.5
179 cm^{-1} . The spectrometer is calibrated with a silicon wafer.

180 *2.5 Electrochemical measurements*

181 Electrochemical measurements are carried out at RT in a home-made three electrode Teflon
182 cell connected to a potentiostat (Biologic SP-300). A reversible hydrogen electrode (RHE)
183 designed for alkaline medium (Hydroflex purchased by Gaskatel) and a glassy carbon (GC) slab
184 are used as reference and counter electrodes, respectively. The working electrode is a 5 mm
185 diameter GC disk (geometric surface area of 0.196 cm^2). A catalytic ink is prepared by
186 dispersing 20 mg of catalytic powder into a solution composed of 500 μL of ultra-pure water
187 (Millipore), 500 μL of isopropanol (Sigma-Aldrich, 99.5%) and 100 μL of Nafion (Sigma
188 Aldrich, 5 wt. % in lower aliphatic alcohols). The ink is homogenized by ultrasonication for 15
189 min. 3.8 μL of the catalytic ink is deposited onto the glassy carbon disc to reach a catalyst
190 loading of 0.35 mg cm^{-2} and allowed to dry under N_2 (U, Air liquide) atmosphere at room
191 temperature. All measurements are performed in a nitrogen saturated 1 mol L^{-1} KOH electrolyte
192 ($\geq 85\%$, Sigma Aldrich). Cyclic voltammograms and polarization curves are recorded between
193 0.15 and 1.5 V vs. RHE and between 0.8 and 1.8 V vs. RHE, respectively. Polarization curves
194 are recorded by applying a rotation rate of 1600 rpm to the rotating disk electrode. IR drop
195 correction of polarization curves is applied. The cell resistance is determined by electrochemical
196 impedance spectroscopy (EIS) in the capacitive region. EIS experiments are also carried out at
197 different electrode potentials in the OER region (potential range from 1.5 to 1.8 V vs. RHE). All
198 EIS measurements are recorded with an oscillation amplitude of 10 mV. Impedance spectra are
199 acquired in the 100 kHz to 0.1 Hz region using a Biologic SP-300 potentiostat. Acquired spectra
200 are fitted using the Z-Fit plug-in from EC-lab software (version 11.43).

201 The same experimental cell is used for stability tests, but the working electrode is a 2 cm²
202 geometric surface area nickel foam (Goodfellow, porosity of 95%, purity of 99.5%) impregnated
203 by a catalytic ink containing 40 mg of catalytic powder, 1000 μL of isopropanol, 1000 μL of
204 ultra-pure water and 300 μL of Nafion solution (5wt. % in a mixture of lower aliphatic alcohols).
205 Stability tests are performed in N₂-purged 1 M and 5 M KOH electrolytes. Chronopotentiometric
206 measurements are performed by applying a constant current of 20 mA (current density of 10 mA
207 cm⁻²_{geo}).

208 *In situ* Raman spectroscopy measurements are performed in a home-made electrochemical cell
209 equipped with a reference hydrogen electrode (purchased by Gaskatel company), a counter
210 electrode (glassy carbon slab) and a working electrode (glassy carbon disk with a diameter of 5
211 mm). The working electrode is prepared in the same way as for the cyclic voltammetry
212 measurements (see above). Before recording Raman spectra, the catalyst is cycled 100 times
213 between 0.8 and 1.45 V *vs.* RHE to stabilize the catalytic surface. To get a better signal, Raman
214 spectra are recorded without any window as described in reference [54]. A long-distance
215 microscope objective (Olympus 50x) is used. A 514 nm exciting wavelength is employed and the
216 power of the laser source is set at 4 mW. Spectra are acquired using a diffraction grating with
217 1800 grooves mm⁻¹ and a confocal hole of 200 μm. The Labspec 5 software is used for the
218 acquisition of spectra as well as for the analysis of experimental data.

219

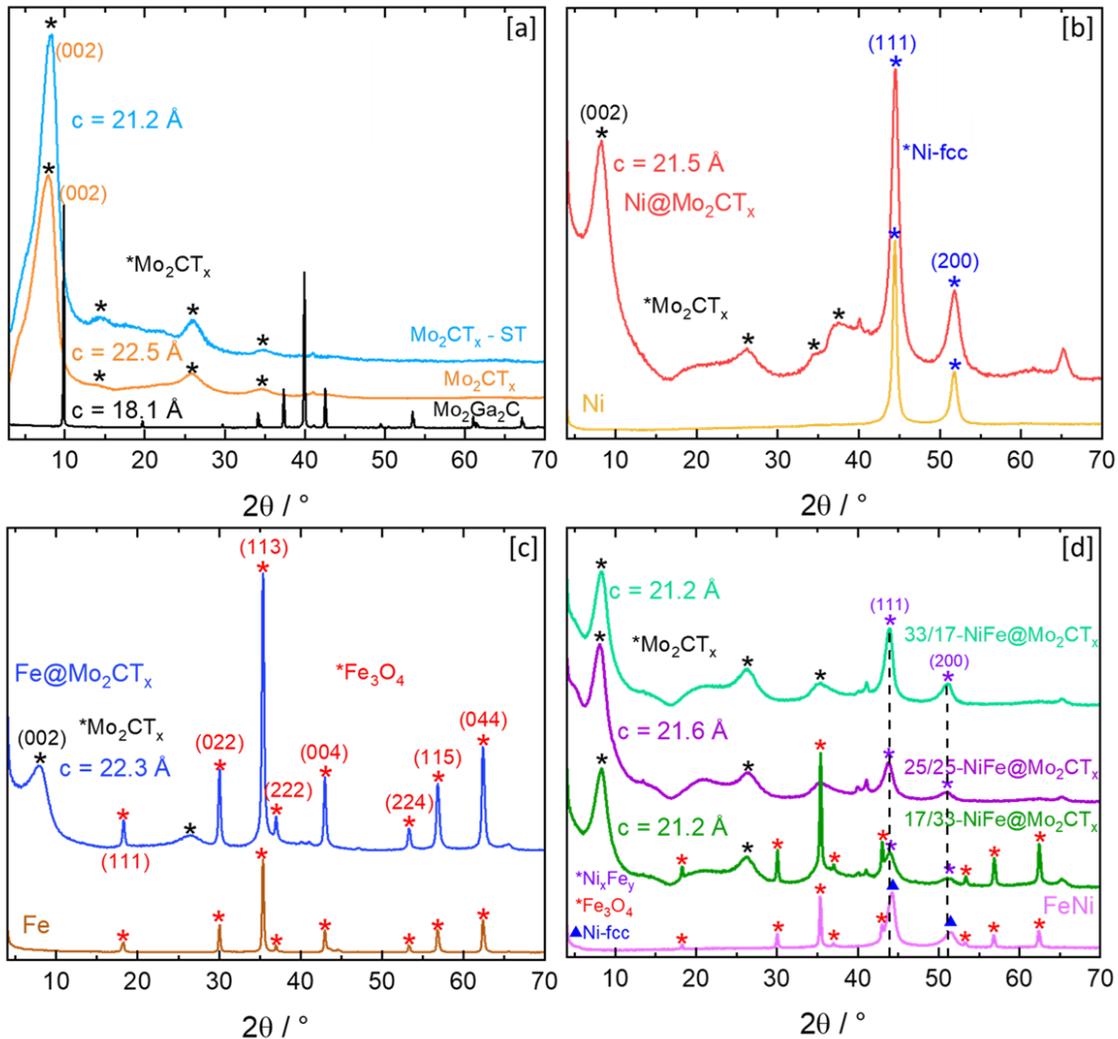
220 **3. Results and discussion**

221 3.1 Characterization of materials

222 The Mo₂CT_x MXene support has been synthesized by exfoliation of the Mo₂Ga₂C MAX like-
223 phase followed by delamination in TBAOH and then, the Ni_xFe_y@Mo₂CT_x materials by a

224 polyol-assisted solvothermal synthesis route. The polyol-assisted solvothermal procedure has
225 also been applied to the MXene alone (referred to as $\text{Mo}_2\text{CT}_x\text{-ST}$) to further investigate possible
226 induced structural changes. At last, unsupported Ni, Fe and NiFe catalysts have been synthesized
227 to compare their structure with those of the MXene-supported ones. All experimental X-ray
228 diffraction patterns are plotted in Figure 1.

229 The XRD pattern of the $\text{Mo}_2\text{Ga}_2\text{C}$ powder is given in Figure 1a. A phase purity of 97.3(2) % is
230 estimated from the Rietveld refinement performed on the XRD pattern in the 5-120° angular
231 range (data not shown), the impurities corresponding to 0.6(2) % of $\alpha\text{-Mo}_2\text{C}$ and 2.1(1) % of
232 Mo_2GaC . For the Mo_2CT_x and $\text{Mo}_2\text{CT}_x\text{-ST}$ materials (Figure 1a), the absence of the sharp
233 diffraction peak at 9.9 ° evidences the formation of a pure MXene phase validating the selected
234 procedure to separate the unreacted $\text{Mo}_2\text{Ga}_2\text{C}$ MAX-like phase from the MXene during the
235 polyol-assisted solvothermal process. This fact is further confirmed by ICP-OES analysis of the
236 MXene powder that reveals a very low amount of Ga (0.03 Ga atom for 2 Mo atoms). For the
237 Mo_2CT_x MXene sample, the c parameter value of the hexagonal lattice calculated from the
238 position of the broad (002) diffraction peak is about 22.5 Å, in agreement with already reported
239 values [51]. For the $\text{Mo}_2\text{CT}_x\text{-ST}$ sample, the value of the c parameter is ca. 21.2 Å, *i.e.*, very
240 close to the value obtained for the pristine Mo_2CT_x (22.5 Å). As described in a previous work
241 [55], the interstratification phenomenon often at stake with MXene leads to noticeable variation
242 on the c parameter due to hydration heterogeneities in-between the sheets. Herein, no significant
243 modification of the interlayer spacing value was observed and consequently it can be stated that
244 the polyol-assisted solvothermal treatment has little impact on the MXene structure.



245 **Figure 1.** X-ray diffraction patterns recorded for: (a) $\text{Mo}_2\text{Ga}_2\text{C}$, Mo_2CT_x and $\text{Mo}_2\text{CT}_x\text{-ST}$; (b)
 246 Ni and $\text{Ni@Mo}_2\text{CT}_x$ (c) Fe and $\text{Fe@Mo}_2\text{CT}_x$; (d) $\text{33/17-NiFe@Mo}_2\text{CT}_x$, $\text{25/25-NiFe@Mo}_2\text{CT}_x$,
 247 $\text{17/33-NiFe@Mo}_2\text{CT}_x$ and FeNi materials.
 248

249 For MXene-supported Ni_xFe_y materials (Figures 1b to 1d), the c parameter values of the
 250 Mo_2CT_x support lie between 21.5 and 22.3 Å, confirming again that non-significant changes in
 251 the chemical nature of molecules and ions intercalated in the interlayer spacing occur during the
 252 synthesis process. Moreover, no diffraction peak corresponding to molybdenum oxides could be
 253 identified, showing that the MXene is not oxidized, which is not so surprising since the synthesis
 254 is performed in a reducing environment (ethylene glycol). This observation is of utmost

255 importance since the preservation of the MXene structural properties (and thus of its electronic
256 conductivity) is mandatory to obtain efficient heterostructured electrocatalysts. This point is
257 often neglected in literature where for numerous composite catalysts recently reported, the
258 MXene support was strongly oxidized during the synthesis [56, 57].

259 Regarding the XRD patterns of single metal (Fe or Ni) unsupported samples, features
260 corresponding to Ni-fcc phase (01-089-7128 JCPDS file) and Fe₃O₄ spinel phase (98-008-2453
261 JCPDS file) are observed. The diffraction pattern of the unsupported FeNi material (Fig. 1d) is
262 only a linear combination of those recorded for unsupported Ni and Fe materials (Figure 1b and
263 1c), *i.e.*, a mixture of Ni-fcc and Fe₃O₄ phases; no alloyed phase of Fe and Ni elements could be
264 identified. These phases are also observed in the Ni@Mo₂CT_x and Fe@Mo₂CT_x samples,
265 respectively, in addition to that of the MXene. Interestingly, the diffraction patterns of the 25/25-
266 NiFe@Mo₂CT_x and 33/17-NiFe@Mo₂CT_x materials (Figure 1d) do not show any signal of the
267 Fe₃O₄ phase but a shift of the 111 and 200 diffraction peaks of fcc-Ni phase towards lower
268 angles testifies the presence of a new single face centered cubic Ni_xFe_y nanoalloy phase in
269 agreement with the incorporation of iron in the Ni-fcc phase (metal radii are 126 pm and 124 pm
270 for Fe and Ni, respectively). The Ni-Fe phase diagram predicts indeed the existence of a large fcc
271 solid solution above 30 mol% of nickel [58]. For the 17/33-NiFe@Mo₂CT_x sample (Figure 1d),
272 the signature of Fe₃O₄ phase can again be observed. For Fe-rich materials, the reducing
273 conditions are not strong enough to force the iron element to participate to the nanoalloy
274 germination-growth. As a conclusion, the transition from homogeneous to heterogeneous
275 germination when Mo₂CT_x is introduced may favor the stabilization and thus the growth of
276 Ni_xFe_y nanoalloys, a clear advantage to get a highly efficient electrocatalyst as discussed latter in
277 this manuscript.

278 The crystallite sizes of Fe_3O_4 and Ni catalysts are estimated using Scherrer's law [59]. The full
279 width at half maximum was determined by assuming Lorentzian line profiles and the
280 instrumental width determined using a LaB_6 standard powder is subtracted. The crystallite sizes
281 of unsupported Ni and Fe_3O_4 materials are ca. 27 nm and ca. 45 nm, respectively. The crystallite
282 size of Ni and Fe_3O_4 catalysts in $\text{Ni@Mo}_2\text{CT}_x$ and $\text{Fe@Mo}_2\text{CT}_x$ composites are ca. 13 and ca. 35
283 nm, respectively, indicating a lower crystallinity than for the unsupported ones.

284 Particle size distributions of Fe_3O_4 and Ni catalysts was established by measuring 100 particles
285 from high magnification TEM images (Figure S1). For unsupported Ni and Fe samples the mean
286 particle sizes are ca. 123 and ca. 57 nm, respectively, whereas for $\text{Ni@Mo}_2\text{CT}_x$ and $\text{Fe@Mo}_2\text{CT}_x$
287 samples they are ca. 17 and ca. 40 nm, respectively. The nucleation process is energetically
288 favored in the presence of the MXene support (heterogeneous nucleation) allowing multiplying
289 the number of nucleation sites and enabling the probable formation of smaller particles than in
290 the case of homogeneous nucleation leading to unsupported particles.

291 The crystallite sizes of Ni_xFe_y catalysts in 25/25- $\text{NiFe@Mo}_2\text{CT}_x$, 33/17- $\text{NiFe@Mo}_2\text{CT}_x$ and
292 17/33- $\text{NiFe@Mo}_2\text{CT}_x$ samples are ca. 12, 12 and 16 nm, respectively. Because the 17/33-
293 $\text{NiFe@Mo}_2\text{CT}_x$ sample contains both Ni_xFe_y and Fe_3O_4 phases, it is not possible to discriminate
294 the size of Fe_3O_4 and Ni_xFe_y particles from TEM images. The mean particle sizes are thus only
295 determined for the 25/25- $\text{NiFe@Mo}_2\text{CT}_x$ and 33/17- $\text{NiFe@Mo}_2\text{CT}_x$ samples (Figure S1). For
296 both samples, mean particle sizes are much greater than crystallite sizes (for example, mean
297 particle size of 60 nm and crystallite size of 12 nm for the 33/17- $\text{NiFe@Mo}_2\text{CT}_x$ samples). This
298 probably results from the formation of polycrystalline particles. Anyway, the very small
299 crystallite sizes calculated for both composites tend to confirm that the presence of the MXene

300 support favors the nucleation step at the expense of the growth step, leading to the formation of
301 Ni_xFe_y nanoalloys rather than to phase segregations.

302 SEM experiments are performed to investigate the morphology of the different materials.
303 Scanning electron micrographs of $\text{Mo}_2\text{Ga}_2\text{C}$, Mo_2CT_x MXene and 25/25-NiFe@ Mo_2CT_x are
304 shown in Figure S2. $\text{Mo}_2\text{Ga}_2\text{C}$ exhibits a typical platelet morphology with crystals that have a
305 lateral size ranging from 1 to 10 microns (Figures S2a and S2b) [60, 61] while the Mo_2CT_x
306 sample (Figures S2c and S2d) exhibits a typical film-like morphology. Sheets formed by
307 Mo_2CT_x multi-layers with intersheet gaps (Figures S2d) display a relatively smooth surface
308 (Figures S2c), and the different multi-layers are more or less wrapped owing to the restacking of
309 delaminated MXene sheets after filtration [60-63]. After the polyol-assisted solvothermal
310 synthesis of composite materials, the sheets appear coated by aggregated Ni_xFe_y nanoparticles
311 both on the top surface and on the edge of Mo_2CT_x layers constituting the sheets (Figures 2e and
312 2f for the 25/25-NiFe@ Mo_2CT_x composite). Large scale elemental mapping analyses were
313 performed on 25/25-NiFe@ Mo_2CT_x , 33/17-NiFe@ Mo_2CT_x and 17/33-NiFe@ Mo_2CT_x samples
314 (Figure S3). Spectral regions associated to the combination of all elements, Ni, Fe and Mo
315 elements were specifically analyzed. Regarding the combination of elements (Figure S3b), it is
316 clear that 17/33-NiFe@ Mo_2CT_x contains two different kinds of particles: those only composed
317 of Fe, associated to Fe_3O_4 phase and those composed of a combination of Ni and Fe elements,
318 associated to Ni_xFe_y nanoalloy. Only the presence of alloyed particles can be observed with other
319 samples in agreement with XRD characterizations.

320

321

322 The chemical compositions of the different materials have been determined by ICP-OES. Mo,
 323 Ni and Fe elements were quantified and results are given in Table 2.

324

325 **Table 2:** Chemical composition of supported and unsupported materials determined by
 326 ICP-OES. Nominal Ni/Fe molar ratio corresponds to the ratio expected from the introduced
 327 amounts of metal salts.

328

Sample	wt. %				Nominal Ni/Fe molar ratio	Experimental Ni/Fe molar ratio
	Mo	Ni	Fe	Mo ₂ C(OH) ₂		
Ni	-	91.6	-	-	-	-
FeNi	-	55.4	29.5	-	0.95	1.79
Fe	-	-	78.6	-	-	-
Ni@Mo ₂ CT _x	21.4	59.2	-	26.5	-	-
Fe@Mo ₂ CT _x	15.1	-	52.3	18.7	-	-
33/17-NiFe@Mo ₂ CT _x	29.7	38.0	9.0	36.8	1.90	4.02
25/25-NiFe@Mo ₂ CT _x	33.8	29.9	10.7	41.9	0.95	2.66
17/33-NiFe@Mo ₂ CT _x	21.3	20.4	32.3	26.4	0.47	0.60
Mo ₂ CT _x -ST	63.6	-	-	78.8	-	-

329

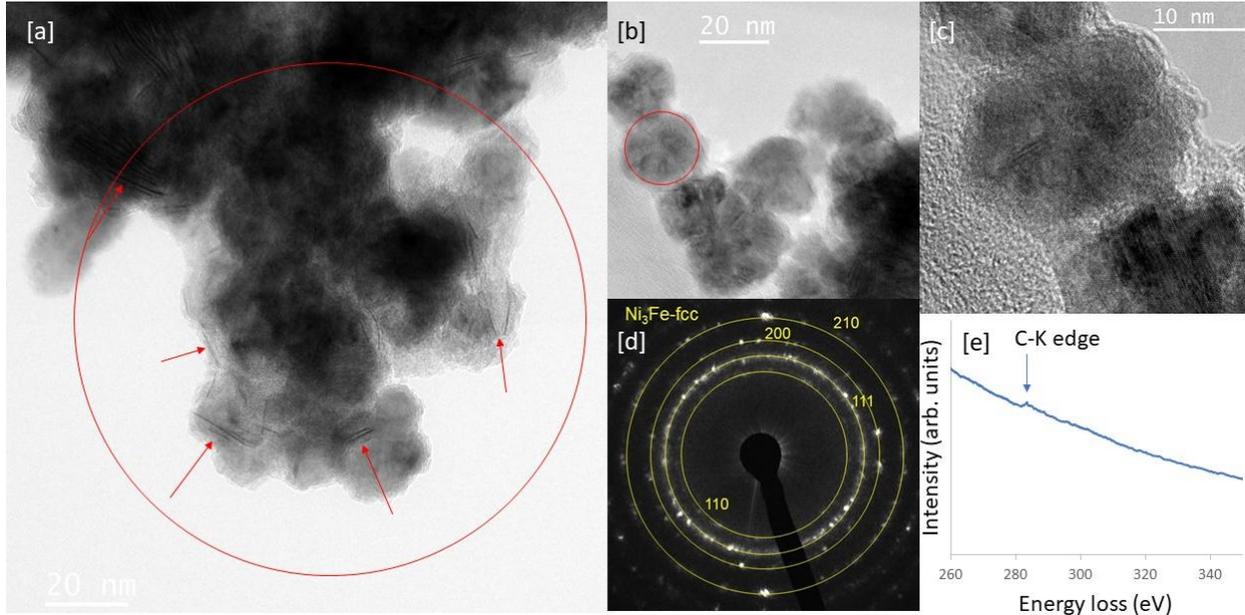
330 The targeted loadings for MXene in composites materials (50 wt.%) are calculated assuming
 331 the chemical formula Mo₂C(OH)₂ with a molar mass of 237.89 g mol⁻¹. This chemical formula
 332 does not consider water and cations (TBA⁺) potentially inserted in the multi-layers of MXene
 333 sheets, explaining that the calculated MXene loadings remain always lower than the targeted
 334 ones. For 17/33-NiFe@Mo₂CT_x and Fe@Mo₂CT_x materials, the oxygen content drastically
 335 increases due to the presence of the Fe₃O₄ phase as evidenced by XRD measurements (Figure 1),
 336 leading to a bias in the quantification. In addition, some molecules from the solvents used for the
 337 polyol-assisted solvothermal synthesis and the washing steps probably remain trapped between
 338 the MXene sheets and/or in the interstices of Ni_xFe_y nanoparticle agglomerates, which for
 339 instance could explain the value of 92 wt.% for the unsupported Ni sample instead of 100 wt.%.
 340 For materials with bimetallic Fe-Ni catalysts, the experimental Ni/Fe ratio is systematically and
 341 in a reproducible manner (Ni/Fe ratio similar from one synthesis to another one) higher than the

342 expected one suggesting a systematic loss of iron during the synthesis procedure. However, the
343 reproducibility ensures the control of the final ratio in the materials.

344 Raman spectroscopy is used to investigate the oxidation state of the MXene and the chemical
345 nature of terminal groups. Raman spectra are acquired in the $85 - 830 \text{ cm}^{-1}$ spectral range for the
346 $\text{Mo}_2\text{Ga}_2\text{C}$, Mo_2CT_x , $\text{Mo}_2\text{CT}_x\text{-ST}$ and $25/25\text{-NiFe@Mo}_2\text{CT}_x$ samples (Figure S4). No peaks
347 corresponding to molybdenum oxide is identified, confirming that the MXene surface is not
348 oxidized during the nucleation and growth of Ni_xFe particles. However, the polyol-assisted
349 solvothermal procedure affects noticeably the nature of the terminal groups of the MXene by
350 replacing fluorine with oxygenated groups. Details on the Raman study and assignment of peaks
351 can be found in the ‘Raman spectroscopy’ section of the supplementary information.

352 The microstructure and chemistry of the $25/25\text{-NiFe@Mo}_2\text{CT}_x$ material (the most efficient
353 material for the OER, see further) is investigated by TEM/EF-SAED (Figures 2a to 2d) and
354 EELS (Figure 2e). Figure 2a displays a dense network of nanoparticles, Figures 2b and 2c focus
355 on several particles to observe their general shape and size. Dark lines (highlighted by arrows)
356 are ascribed to small MXene sheets, in agreement with the detection of the C-K edge by EELS
357 (Figure 2e), although the signal is very low probably due to the small amount of Mo_2CT_x sheets
358 in the irradiated area delimited by the red circle (a defocused electron beam is used to minimize
359 beam damage). The Feret’s diameter of Ni_xFe_y nanoparticles is estimated to ca. 20 nm, in
360 agreement with XRD and TEM characterizations. The typical EF-SAED pattern in Figure 3d is
361 correctly indexed considering a $\text{Ni}_x\text{Fe}_y\text{-fcc}$ structure, confirming the XRD results. The analysis
362 of Fe-L_{2,3} and Ni-L_{2,3} edges from EELS measurements (shown in Figure S9 for comparison with
363 characterization of aged materials) leads to particle composition between $\text{Ni}_{2.9}\text{Fe}$ and $\text{Ni}_{3.7}\text{Fe}$, in
364 agreement with ICP measurements ($\text{Ni}_{2.66}\text{Fe}$) considering the uncertainty on the quantifications.

365



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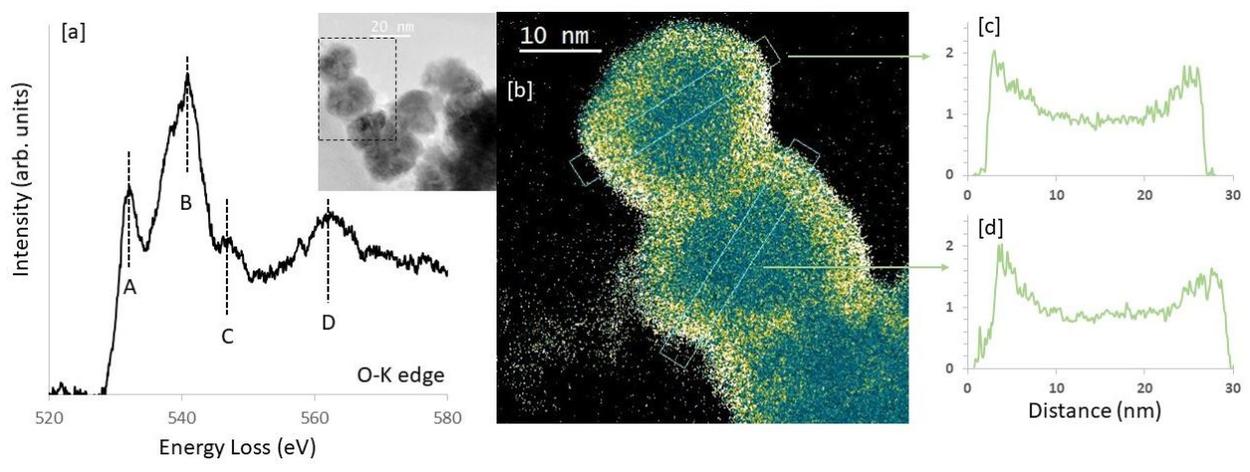
367 **Figure 2:** (a) to (c) micrographs recorded on different areas of a TEM grid prepared from the
368 25/25-NiFe@Mo₂CT_x sample. In (a) arrows identify elongated contrasts, (c) gives a
369 magnification of the nanoparticle highlighted in red in (b), (d) typical energy-filtered selected
370 area diffraction pattern showing that nanoparticles essentially have a fcc-Ni_xFe structure and (e)
371 C-K edge recorded using EELS on the area identified by a red circle in (a).

372

373 Chemical analysis performed by EELS point out the presence of a non-negligible amount of
374 oxygen in the sample (Figure 3a). The O-K edge exhibits a well-defined fine structure with a
375 main peak B and different signatures of lower intensity labelled A, C and D, very similar to that
376 reported on NiFe₂O₄ [64, 65]. Energy-Filtered TEM (EFTEM) at the O-K edge using the jump
377 ratio method is used to map the oxygen distribution in nanoparticles (Figures 3b). Clearer areas
378 evidence oxygen enrichment around the particles. Intensity profiles extracted through two
379 particles and integrated over 30 pixels (Figures 3c and 3d) clearly show oxygen enrichment on
380 the outer edge of the nanoparticles. This result is not surprising since metallic alloys such as
381 Ni_xFe_y are subject to surface oxidation when exposed to air. The low thickness of the shell and

382 the oxygen concentration gradient from bulk to surface of the nanoparticles indicate that this
 383 oxide is rather amorphous, and therefore not detectable by XRD. Moreover, the Raman spectrum
 384 of the material (Figure S4) does not exhibit any visible vibrational feature corresponding to the
 385 nearly spinel-like phase shell surrounding Ni_xFe_y nanoparticles observed by TEM-EELS
 386 technique, likely owing to the lack of long-range ordering and/or the low amount of matter
 387 composing this shell.

388



389

390 **Figure 3.** (a) Typical O-K edge recorded in various areas of the 25/25-NiFe@Mo₂CT_x sample.
 391 (b) EFTEM micrograph at the O-K edge recorded using the jump ratio method (white areas
 392 evidence oxygen enrichment on the outer part of the nanoparticles) and (c) corresponding
 393 intensity profiles extracted along the two directions evidenced by the rectangles (intensities were
 394 integrated over 30 pixels).
 395

396 3.2 Electrochemical measurements

397 The electrochemical behavior of the different composite materials was investigated and
 398 compared to that of Mo₂CT_x-ST. Figure 4a presents the first voltammetric cycles recorded
 399 between 0.1 and 1.55 V vs. RHE in a nitrogen-purged 1 M KOH supporting electrolyte on the
 400 different materials.

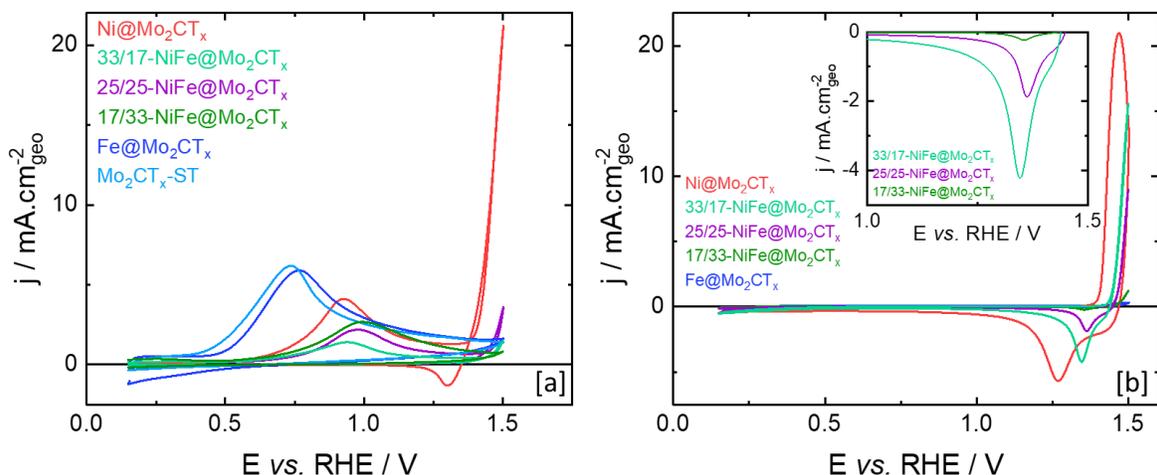
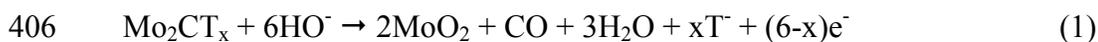


Figure 4. (a) First cyclic voltammogram recorded with the different composite materials ($\text{Ni@Mo}_2\text{CT}_x$, $\text{Fe@Mo}_2\text{CT}_x$, $17/33\text{-NiFe@Mo}_2\text{CT}_x$, $25/25\text{-NiFe@Mo}_2\text{CT}_x$ and $33/17\text{-NiFe@Mo}_2\text{CT}_x$) and $\text{Mo}_2\text{CT}_x\text{-ST}$ MXene. (b) 100th voltammogram recorded with $\text{Fe@Mo}_2\text{CT}_x$, $17/33\text{-NiFe@Mo}_2\text{CT}_x$, $25/25\text{-NiFe@Mo}_2\text{CT}_x$ and $33/17\text{-NiFe@Mo}_2\text{CT}_x$ and $\text{Ni@Mo}_2\text{CT}_x$. All voltammograms are recorded in a nitrogen saturated KOH 1 M electrolyte. The scan rate is set at 50 mV s^{-1} .

401 In all cases, an irreversible oxidation peak is rising between 0.5 and 1.0 V vs. RHE in the
 402 positive going scan, which is due to the oxidation of the material surface. Because this oxidation
 403 peak also appears for Mo_2CT_x alone, it is ascribed to the oxidation of the MXene according, by
 404 analogy with the recently reported electrochemical behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ [42, 43], to the following
 405 equation:



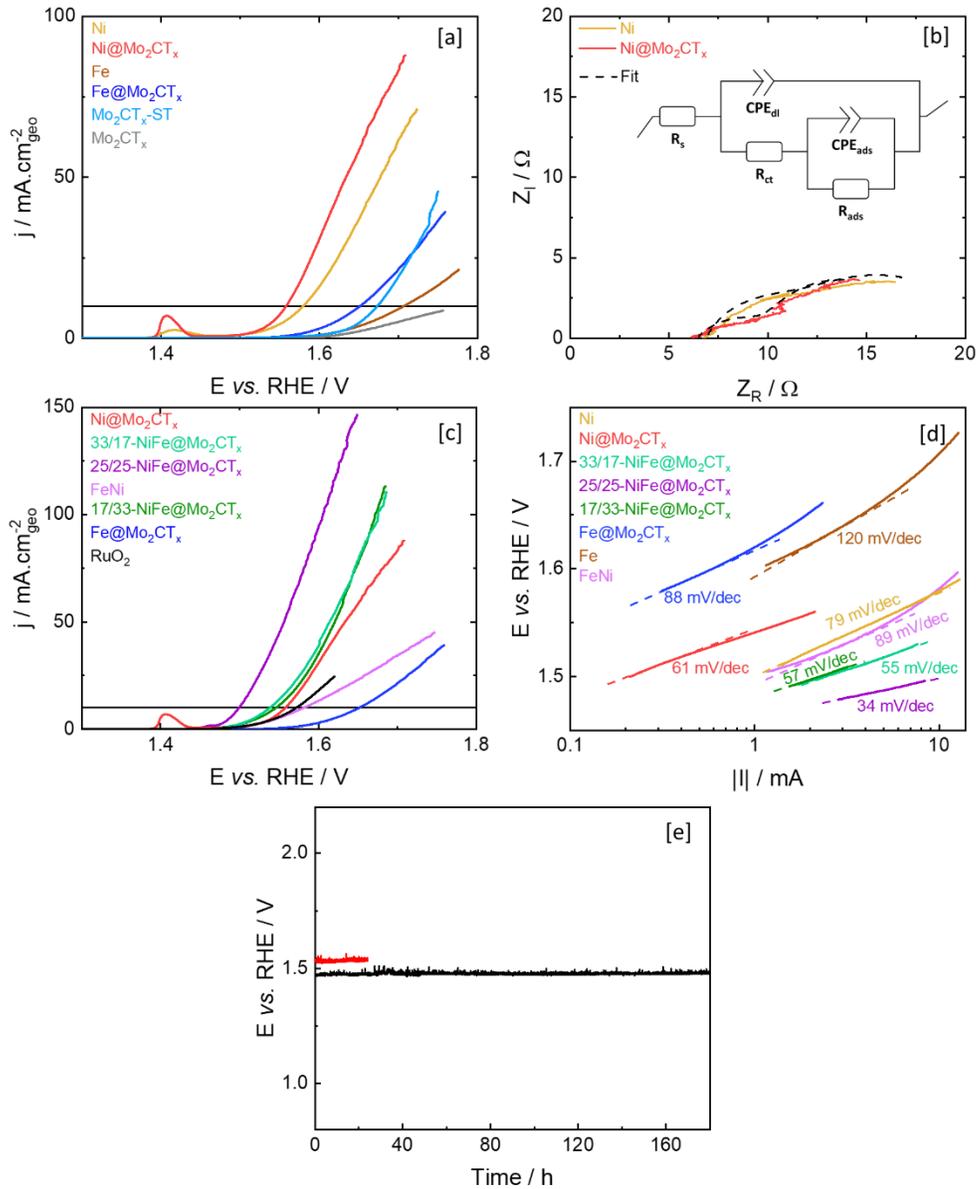
407 Electrochemical signatures of Mo_2CT_x and $\text{Mo}_2\text{CT}_x\text{-ST}$ are quite similar (Figure S5). The
 408 presence of the irreversible oxidation peak indicates that MXene surface is not oxidized in course
 409 of the polyol-assisted solvothermal synthesis in accordance with previous characterizations, and
 410 thus redox properties of Mo atoms are kept. The coulometry in the irreversible oxidation peak of
 411 $\text{Mo}_2\text{CT}_x\text{-ST}$ seems to be higher than that of Mo_2CT_x . It is likely that the polyol-assisted
 412 solvothermal treatment favors delamination of MXene sheets, leading to increase the surface of

413 MXene exposed to the electrolyte. In a catalytic point of view, an increase of the support specific
414 surface area is very positive for a higher dispersion of the active phase.

415 The position of the irreversible oxidation peak of Fe@Mo₂CT_x, Ni@Mo₂CT_x 33/17-
416 NiFe@Mo₂CT_x, 25/25-NiFe@Mo₂CT_x and 17/33-NiFe@Mo₂CT_x materials is shifted towards
417 higher potentials: 0.77, 0.93, 0.93, 0.98 and 0.99 V vs. RHE, respectively, against 0.73 V vs.
418 RHE for Mo₂CT_x-ST. The presence of the active phase stabilizes the MXene surface and delays
419 its oxidation [66, 67], possibly due to changes in electron density of state of the surface Mo
420 atoms. Ni@Mo₂CT_x produces a large oxidation wave at potentials higher than 1.4 V vs. RHE in
421 the positive potential scan and a reduction peak at 1.3 V vs. RHE in the negative scan,
422 corresponding to Ni²⁺/Ni³⁺ redox transition.

423 The irreversible MXene oxidation signal doesn't appear in the second voltammetric cycle
424 (Figure S6), indicating that the surface of the MXene exposed to the electrolyte is totally
425 passivated in the first cycle. However, the Ni_xFe_y active phases need several voltammetric cycles
426 to give stable electrochemical signatures (data not shown). Figure 4b presents the 100th
427 voltammetric cycle recorded on each material. No signal of iron redox transition is observed on
428 the voltammogram of Fe@Mo₂CT_x, in agreement with literature [68-70]. On contrary,
429 Ni@Mo₂CT_x leads to well-defined redox signals centered at ca. 1.46 V (oxidation) and 1.28 V
430 (reduction) vs. RHE corresponding to the Ni(OH)₂/NiOOH transition. For nickel-iron based
431 composites, the Ni²⁺/Ni³⁺ oxidation wave is shifted towards higher potentials and overlaps with
432 the OER current, and the reduction peak appears at ca. 1.36, 1.37 V and 1.34 V vs. RHE for
433 17/33-NiFe@Mo₂CT_x, 25/25-NiFe@Mo₂CT_x and 33/17-NiFe@Mo₂CT_x, respectively, i.e., at
434 potential 60 to 90 mV higher than that for Ni@Mo₂CT_x. The stabilization of Ni²⁺ state, thanks to

435 the presence of iron [22], induces an increase of the oxidizing power of nickel species formed at
 436 potentials of the OER, and thus the enhancement of the OER activity (see below).



437 **Figure 5.** (a) Polarization curves recorded with different materials in nitrogen-purged 1 M KOH
 438 electrolyte. (b) Impedance spectra recorded at 1.60 V vs. RHE for Ni and Ni@Mo₂CT_x samples
 439 and equivalent circuit model used to fit experimental electrochemical impedance spectra. (c)
 440 Polarization curves recorded on supported composites and FeNi sample in nitrogen-purged 1 M
 441 KOH. (d) Tafel plots determined from polarization curves presented in (a) and (c). (e)
 442 Chronopotentiometry performed on the 25/25-NiFe@Mo₂CT_x material in nitrogen-purged 1 M
 443 KOH (red) and 5 M KOH (black) electrolytes, $i = 20$ mA (current density of $10 \text{ mA cm}^{-2}_{\text{geo}}$).

444 The OER activity of the materials is investigated in 1 M KOH aqueous medium by recording
445 polarization curves in the 1.2 V to 1.8 V *vs.* RHE potential range (Figure 5a). The OER activity
446 of Mo₂CT_x-ST appears higher than that for Mo₂CT_x sample owing to the larger electrochemical
447 surface area of Mo₂CT_x-ST MXene (higher coulometry for Mo oxidation – Figure S5) than that
448 of the Mo₂CT_x sample (Figure S5). Ni@Mo₂CT_x and Fe@Mo₂CT_x composites are more active
449 than the corresponding unsupported Ni and Fe catalysts, although their Ni and Fe contents are
450 drastically lower (Table 2). A current density of 10 mA cm⁻²_{geo} is reached at 1.56 V and 1.65 V
451 *vs.* RHE for Ni@Mo₂CT_x and Fe@Mo₂CT_x, respectively, against 1.58 V and 1.71 V *vs.* RHE for
452 unsupported Ni and Fe catalysts, respectively. The promotional effect of the MXene support can
453 originate from the induced lower Ni and Fe mean particle sizes than in the case of non-supported
454 Ni and Fe catalysts, leading to higher electroactive surface area (ESCA) of supported materials,
455 and/or from a strong MXene/active phase interaction promoting charge transfer and increasing
456 OER activity.

457 The determination of the ESCA of such materials is not always possible (“Discussion on the
458 determination of ECSA value” section in supplementary information). The most reliable
459 technique consists to estimate the Ni ECSA in samples through the coulometry associated with
460 the one electron reduction of NiOOH into Ni(OH)₂. But this method cannot be used for Fe-based
461 samples (no coulometry due to Fe redox) or NiFe-based samples since redox properties of Ni are
462 altered (stabilization of Ni²⁺) in the presence of iron (Figure 5). Therefore, ESCAs have been
463 determined only for non-supported Ni and Ni@Mo₂CT_x materials. From voltammograms in
464 Figure S8a, and considering a charge of 257 μC cm⁻² for the Ni²⁺/Ni³⁺ redox process occurring
465 on a flat smooth nickel electrode [71, 73], ESCAs were calculated and normalized polarization
466 curves drawn (Figure S8b). Both materials lead to similar surface activity, meaning that size

467 effect cannot be neglected. The charge transfer resistance for the OER is estimated from
 468 electrochemical impedance spectra at 1.6 V vs. RHE, after fitting of the data based on the
 469 Armstrong-Henderson equivalent circuit (Figure 5b) [74]. R_s corresponds to the cell resistance
 470 (resulting from electrical connections, electrolyte, and catalytic deposit) and the CPE_{dl} constant
 471 phase element models the double-layer capacitance taking into account the surface roughness
 472 and non-uniform distribution of active sites [75]. R_{ct} and R_{ads} represent the charge transfer
 473 resistance and the mass transfer resistance associated to adsorbed intermediates at the electrode
 474 surface, respectively. The sum of R_{ct} and R_{ads} corresponds to the total faradaic resistance (R_{far}),
 475 which is the descriptor of the kinetics of the OER [76]. CPE_{ads} mimics the charge for the
 476 reversible adsorption of OER intermediates [74]. Values of R_s , R_{ct} , R_{ads} and R_{far} calculated from
 477 the best fit are reported in Table 3.

478

479 **Table 3:** Values of R_s , R_{ct} , R_{ads} and R_{far} parameters obtained by simulating the electrochemical
 480 impedance spectroscopy data.

Sample	R_s (Ω)	R_{ct} (Ω)	R_{ads} (Ω)	R_{far} (Ω)
Ni	6.9	6.5	7.6	14.1
Ni@Mo ₂ CT _x	6.5	4.5	7.4	11.9

481

482 R_s value remains constant (as expected), as well as R_{ads} , whereas R_{far} value is lower for the
 483 Ni@Mo₂CT_x material than that for the non-supported Ni catalyst mainly due to the decrease of
 484 the R_{ct} value. This is an important result that suggests that the passivation (oxidation) of the
 485 MXene does not occur at the interface Ni/MXene support, and that rapid charge transfer between
 486 the Ni active phase and the support is not affected. Another important conclusion is that both
 487 effect, size and charge transfer, are involved in the activity enhancement for the OER of the

488 Ni@Mo₂CT_x material. We can reasonably assume that this is also the case for NiFe@Mo₂CT_x
489 materials.

490 The OER activity of nanocomposites containing both Ni and Fe metals is higher than for
491 Fe@Mo₂CT_x, Ni@Mo₂CT_x catalysts and unsupported NiFe material (Figure 5c). The activity of
492 Ni/Fe mixed composites depends on the iron content with a maximum for the 25/25-
493 NiFe@Mo₂CT_x material containing fcc-Ni_{2.66}Fe particles (Table 2). This material allows
494 reaching 10 mA cm⁻² at a potential of only 1.50 V vs. RHE. The positive impact of Fe on Ni
495 active sites in nanoalloys is known [14, 15, 22, 77-80], but the 25/25-NiFe@Mo₂CT_x material is
496 one of the most efficient MXene-based catalysts ever reported to date (Table S1). Catalysts
497 deposited onto 3D electrodes (Ni foam) can outperform the 25/25-NiFe@Mo₂CT_x material, but a
498 direct comparison of the geometric current density is not fair because the porous structure of Ni
499 foam increase dramatically the specific surface area whereas only projected surface areas is
500 considered to normalize polarization curves. Furthermore, the electrochemical performances
501 obtained herein with 25/25-NiFe@Mo₂CT_x catalyst are better than those obtained with a
502 reference catalyst, a commercial RuO₂ (E_{j10} = 1.57 V vs RHE) (Figure 5).

503 The OER activities of 33/17-NiFe@Mo₂CT_x (containing only Ni_xFe_y nanoparticles) and 17/33-
504 NiFe@Mo₂CT_x (containing a mixture of Ni_xFe_y and Fe₃O₄ particles) are quite similar, but lower
505 than that of the 25/25-NiFe@Mo₂CT_x material: current density of 10 mA cm⁻² at 1.53 V, 1.54 V
506 and 1.37 V vs. RHE, respectively. The Ni_xFe_y nanoalloy in the 33/17-NiFe@Mo₂CT_x material
507 contains less Fe than the 25/25-NiFe@Mo₂CT_x one (Table 2, last column), so that the Ni
508 oxidizing power is decreased (Figure 4b) and hence the OER activity; moreover, larger Ni_xFe
509 particle size (Figure S1) decreases the ESCA and therefore activity. For the 17/33-
510 NiFe@Mo₂CT_x material, the presence of a large amount of inactive Fe₃O₄ phase observed by

511 XRD (Figure 1) means that the active surface area of Ni_xFe_y is lowered, and thus the OER
512 activity. In our case the optimum Ni/Fe ratio is close to 2.66.

513 The Tafel slopes are determined from steady state current density recorded versus applied
514 electrode potential in the low overpotential region (Figure 5d). Tafel slope values are
515 significantly lower for the $\text{Ni@Mo}_2\text{CT}_x$ and $\text{Fe@Mo}_2\text{CT}_x$ materials compared to their respective
516 non-supported catalysts, *i.e.*, an increase in the rate of the determining step owing to an improved
517 charge transfer. The higher activity of Ni and $\text{Ni@Mo}_2\text{CT}_x$ materials observed in Figure 5a is
518 confirmed by the Tafel slope values of 79 and 61 mV dec^{-1} , respectively (against 88 and 120 mV
519 dec^{-1} for Fe and $\text{Fe@Mo}_2\text{CT}_x$ materials, respectively), suggesting the second chemical reaction
520 process as rate determining step [16]. The Tafel slope value of 57 mV dec^{-1} for the 17/33-
521 $\text{NiFe@Mo}_2\text{CT}_x$ materials decreases down to 34 mV dec^{-1} for the 25/25- $\text{NiFe@Mo}_2\text{CT}_x$ one,
522 showing that the rate determining step shifts from the second chemical step to the recombination
523 of adsorbed $-\text{O}$ at the catalytic surface [81]. The surface structure and the arrangement of Ni and
524 Fe atoms in the 25/25- $\text{NiFe@Mo}_2\text{CT}_x$ material favor the formation of O-O bond (last step of the
525 OER mechanism). The Tafel slope value obtained with the 25/25- $\text{NiFe@Mo}_2\text{CT}_x$ material is the
526 lowest ever reported for catalysts consisting of a Ni- and Fe-based active phase supported on a
527 MXene (Table S1). Although E_{j10} values are rather similar for all materials (Table S1), the
528 25/25- $\text{NiFe@Mo}_2\text{CT}_x$ sample will possibly allow driving a current density of 1 $\text{A cm}^{-2}_{\text{geo}}$ (the
529 minimum targeted current density in electrolysis cells) at lower electrode potentials, which is
530 crucial for the large-scale commercialization of alkaline water electrolyzers.

531 The long-term stability of the 25/25- $\text{NiFe@Mo}_2\text{CT}_x$ material is investigated in 1 M and 5 M
532 KOH aqueous electrolyte at RT by chronopotentiometry at the constant current density of 10 mA
533 $\text{cm}^{-2}_{\text{geo}}$ (Figure 5e). The electrode potential remains at a constant value of 1.48 V *vs.* RHE for 7

534 days in a 5 M KOH electrolyte, showing the high stability of the synthesized material and
535 making it a promising catalyst for the implementation of emerging solid electrolyte alkaline
536 electrolyzers. To investigate the nature of the active sites formed at OER potentials, *in situ*
537 Raman spectra were recorded at different electrode potentials (1.30, 1.35, 1.40, 1.45, 1.50, 1.55
538 V vs. RHE) in the 300-1000 cm^{-1} spectral window (Figure 6) on the 25/25-NiFe@Mo₂CT_x
539 sample. The spectrum recorded at 1.3 V vs. RHE (potential higher than the irreversible oxidation
540 potential of Mo₂CT_x) doesn't show any feature corresponding to either molybdenum oxide or to
541 terminal groups grafted on the Mo₂CT_x surface. Three Raman bands appear at *ca.* 487, 573 and
542 690 cm^{-1} for electrode potential between 1.35 V and 1.45 V vs. RHE, which can be ascribed to
543 the doubly degenerated T_{2g} and A_{1g} modes of the spinel phase [54]. For higher potentials, i.e. in
544 the OER potential region, the vibrational features of the spinel phase disappear while two new
545 bands are observed at *ca.* 475 cm^{-1} and 557 cm^{-1} , which can be ascribed to M-O vibrations of Ni
546 oxyhydroxide probably containing also Fe atoms. On the basis of the band positions, it is
547 difficult to discriminate the formation of either γ -Ni(Fe)OOH or β -Ni(Fe)OOH [79].
548 Nevertheless taking into account the intensity ratio of these two bands [82], β -Ni(Fe)OOH is
549 probably formed, implying that β -Ni(Fe)OOH would be the OER active phase.

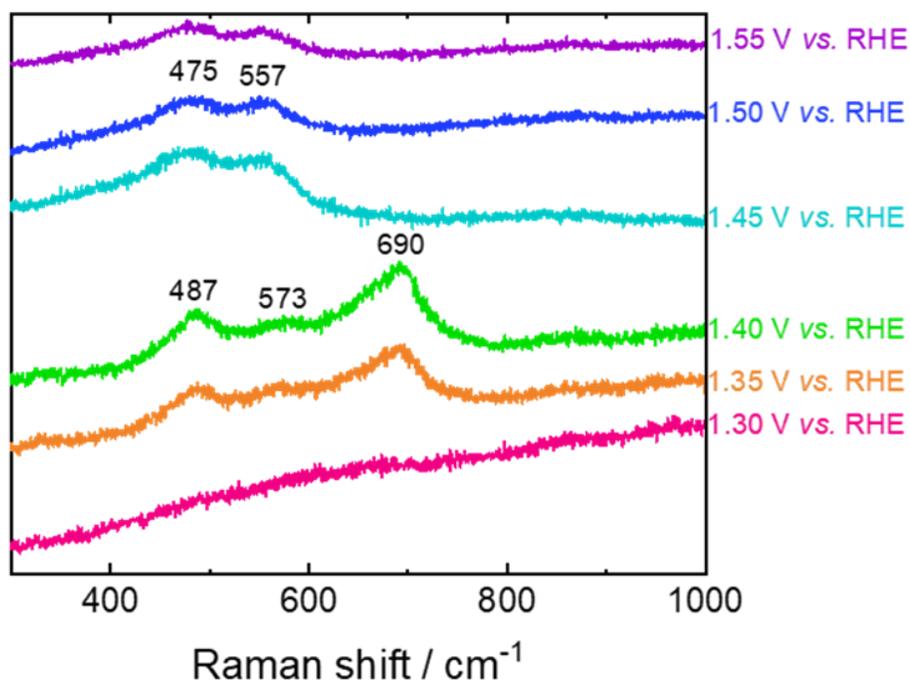
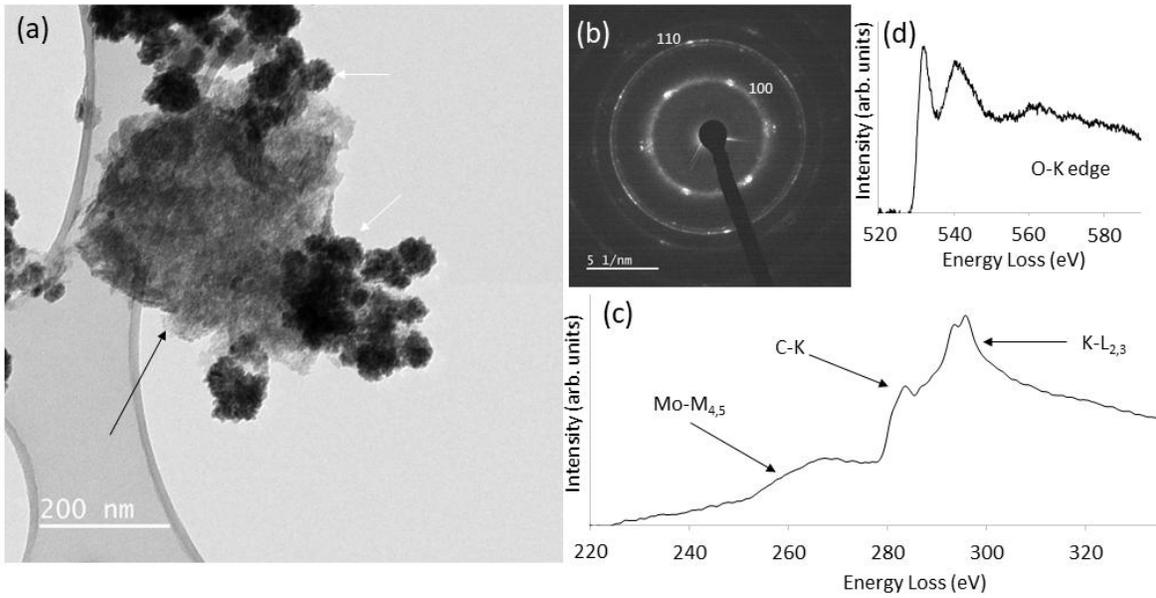


Figure 6. *In-situ* Raman spectra recorded on 25/25-NiFe@Mo₂CT_x catalyst at different electrode potentials. Before recording spectra, the catalyst was cycled 100 times between 0.15 and 1.50 V vs. RHE.

550 The 25/25-NiFe@Mo₂CT material is investigated by TEM-EELS electrode after 100 cycles at
 551 50 mV s⁻¹ between 0.2 and 1.55 V vs. RHE. The TEM image of the aged sample in Figure 7a
 552 display areas with bunches of nanoparticles (white arrows) deposited on the MXene support
 553 (black arrow). EF-SAED of the aged MXene support (Figure 7b) shows rings corresponding to
 554 the original hexagonal structure of Mo₂CT_x. The in-plane unit cell parameter deduced from the
 555 diffraction pattern is around 2.9 Å, in very good agreement with the XRD refinement of Deeva *et*
 556 *al.* [83]. Given the inhomogeneous contrast in Figure 7a and the diffraction pattern, one can
 557 conclude that the MXene sheets are disorganized although their crystallographic structure is
 558 maintained. The chemical analysis by EELS (Figure 7c) evidences the presence of molybdenum
 559 (Mo-M_{4,5} edge), of carbon (C-K edge) and of potassium (K-L_{2,3} edge). The presence of
 560 potassium assesses the fact that this region of the sample was in contact with the KOH
 561 electrolyte and has thus undergone the electrochemical processes. The oxygen K edge (Figure

562 7d) displays fine structures significantly different from those reported by Lajaunie et al. [85] for
 563 different molybdenum oxides (MoO_2 and MoO_3), suggesting that the MXene support has not
 564 been deeply oxidized. All this study shows the MXene support possesses a good chemical
 565 stability during electrochemical cycles.



566
 567 **Figure 7.** (a) TEM micrograph showing the support (black arrow) and the nanoparticles (white
 568 arrows), (b) EF SAED - pattern recorded on the MXene support, (c) EELS spectrum recorded on
 569 the MXene support around the C-K edge, (d) O-K edge recorded on the MXene support.

570
 571 EF-SAED performed on the aged Ni_xFe_y particles (white arrows in Figure 7a) reveal identical
 572 patterns to those obtained before cycling (Figures S9b and S9c), as for EELS measurements
 573 concerning Fe-L_{2,3} and Ni-L_{2,3} edges (Figures S9d and S9e). These results confirm the
 574 reversibility of the oxyhydroxide layer formation previously evidenced by *in situ* Raman
 575 spectroscopy. At last, the O-K edge reveals the presence of oxygen in the nanoparticles with a
 576 fine structure presenting a difference in the relative intensities of the peaks A and B. All these
 577 findings are consistent with a modification of the surface of the nanoparticles inherent to the
 578 modification of their morphology.

579

580

581 **CONCLUSION**

582 A polyol-assisted solvothermal route is proposed to synthesize composite materials consisting
583 of Ni_xFe_y active phases supported on Mo_2CT_x MXene. The synthesis procedure has little effect
584 on the Mo_2CT_x MXene structure and composition. The anchoring sites of the MXene support
585 favor the nucleation and growth of Ni_xFe_y nanoalloys leading to a very efficient active phase
586 towards the OER in alkaline medium. Catalytic properties of Ni_xFe_y are directly related to the
587 Ni/Fe ratio, the most efficient catalyst being obtained for a ratio of 2.66 (25/25-NiFe@ Mo_2CT_x).
588 This material exhibits an outstanding activity with an electrode potential of only 1.50 V vs. RHE
589 for a current density of 10 mA cm^{-2} and a Tafel slope of only 34 mV dec^{-1} . This amazingly low
590 Tafel slope value makes this material a serious candidate to drive current densities required in a
591 real electrolysis cell at low overpotentials and places this catalyst among the best ever reported to
592 date. Thanks to numerous characterization methods, it was highlighted that the high activity of
593 the active phase is mainly due to a combination of 3 factors: the low size of alloyed Ni_xFe_y
594 particles induced by the presence of the MXene in the synthesis reactor, the lower charge transfer
595 resistance between the active phase and the MXene support due to protection of the interface by
596 the Ni_xFe_y particles (active phase/support interaction) and the formation of the active β -
597 Ni(Fe)OOH phase.

598 Long-term experiments have shown that this material also was stable for the OER. TEM-EELS
599 analyses of aged material did not evidence any core oxidation of the MXene, even for potential
600 beyond the irreversible peak potential value. This indicates that only surface Mo atoms are
601 irreversibly oxidized. Under these conditions, MXene sheets are disorganized while keeping
602 their crystallographic structure. Potential cycling experiments indicate a surface reversibility

603 (chemical reset) for Ni_xFe nanoalloys, the oxyhydroxide formed at OER potentials being totally
604 reduced during the negative going scan.

605 Considering the simplicity of the synthesis route and the possibility to tune easily chemical
606 composition of both MXene substrate and active phase, one can reasonably assume that this
607 study paves the way to the emergence of a new class of highly efficient MXene based composite
608 catalysts, thus contributing to the development of energy storage and conversion systems with
609 improved electrical performances.

610

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