

MXene Supported Cobalt Layered Double Hydroxide Nanocrystals: Facile Synthesis Route for a Synergistic Oxygen Evolution Reaction Electrocatalyst

Mohamed Benchakar, Thomas Bilyk, Cyril Garnero, Lola Loupias, Cláudia Morais, Jérôme Pacaud, Christine Canaff, Patrick Chartier, Sophie Morisset,

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An innovative and facile synthesis route to obtain Co-based layered double hydroxide supported onto preserved MXene surface as highly efficient and stable oxygen evolution reaction electrocatalyst is described. The activity and stability of catalyst can be explained by a strong hydroxide/MXene electronic interaction.




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MXene Supported Cobalt Layered Double Hydroxide Nanocrystals: Facile Synthesis Route for a Synergistic **Oxygen Evolution Reaction Electrocatalyst**

Mohamed Benchakar, Thomas Bilyk, Cyril Garnero, Lola Loupias, Claudia Morais, Jérôme Pacaud, Christine Canaff, Patrick Chartier, Sophie Morisset, Nadia Guignard, Vincent Mauchamp,* Stéphane Célérier,* and Aurélien Habrioux* 12

16 The development of reliable electrolyzers is closely related to the development 17 of a cost-effective highly active and stable electrocatalysts for the oxygen 18 evolution reaction (OER). Herein, a simple method is used to synthesize a 19 non-noble metal-based electrocatalyst for OER by synergistically coupling 20 a catalytically active cobalt layered double hydroxide (Co-LDH) with a 21 highly electrically conducting 2D transition metal carbide, Ti₃C₂T_y MXene. 22 23 The synergy between these two bidimensional materials (Co-LDH and 24 $Ti_3C_2T_x$), evidenced by coupling electron energy loss spectroscopy and 25 density functional theory simulations, results in superior electrocatalytic 26 properties and makes possible having an excellent and stable oxygen 27 evolution electrocatalyst. Moreover, the oxidative-sensitive MXene structure 28 is preserved during the synthesis of the composite and the formation of a 29 30 well recovering Co-LDH phase avoids the irreversible oxidation of MXene at 31 high potential values, which may affect its conductivity. With an overpotential 32 of ≈330 mV at a current density of 10 mA cm⁻² the catalyst exhibits a higher 33 catalytic activity toward OER than commercial IrO₂ catalysts. 34

36 37 1. Introduction

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38 The sluggish kinetics of oxygen evolution reaction (OER)^[1] 39 currently hampers the large scale development of many energy 40 storage and conversion devices such as metal-air batteries or 41 42 water electrolyzers required to implement the future energy

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+3 44 45 46 47 48 49 50 51 52 53 54 55 56	M. Benchakar, Dr. C. Garnero, L. Loupias, Dr. C. Morais, C. Canaff, S. Morisset, N. Guignard, Dr. S. Célérier, Dr. A. Habrioux Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP) Université de Poitiers CNRS F-86073 Poitiers, France E-mail: stephane.celerier@univ-poitiers.fr; aurelien.habrioux@univ-poitiers.fr T. Bilyk, Dr. C. Garnero, Dr. J. Pacaud, Dr. P. Chartier, Dr. V. Mauchamp Institut Pprime UPR 3346 CNRS Université de Poitiers ISAE-ENSMA BP 30179, 86962 Futuroscope-Chasseneuil Cedex, France E-mail: vincent.mauchamp@univ-poitiers.fr
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grid.^[2] Finding low-cost, stable, and effi- 15 cient catalysts for the above-mentioned 16 reaction is mandatory for the widespread 17 use of these applications. To date, the most 18 active catalysts reported for OER in acidic 19 media are Ir and Ru-based oxides, which 20 are limited resources in the earth crust.^[3] 21 In alkaline media. 3d transition-metals can 22 also be used as catalysts^[4] since their oxides 23 and hydroxides are thermodynamically 24 stable in such media. As a result, many 25 materials composed of iron, nickel, man-26 ganese, or cobalt are reported as efficient 27 catalysts toward OER.^[5] These 3d transi- 28 tion-metal elements can be combined in 29 numerous crystallographic phases among, which the layered double hydroxide (LDH) 31 family constitutes a good candidate. 32 Indeed cobalt, chromium, nickel, iron, 33 manganese or their alloy based LDH were 34 already reported as efficient catalysts for 35 36

the OER in alkaline media.^[6] LDH can be described by the general formula 37 $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}]^{n-}$, mH₂O where M²⁺ and M³⁺ are 38 respectively divalent and trivalent cations and A^{n-} is the inter-39 layer anion.^[6d] The LDH structure is based on the partial 40 exchange of divalent and trivalent metal cations in the main 41 layer. The positive charge of the main layer is compensated 42 by the intercalation of anions in the interlayer spacing. LDH 43 materials, however, exhibit two major drawbacks. First, the pro-44 posed synthesis routes are complex and involve either the ex 45 situ preparation of zeolitic imidazolate framework-67 (ZIF-67)^[7] 46 or its in situ formation.^[6c] Second, these materials suffer from 47 a poor intrinsic electronic conductivity. To overcome the latter, 48 LDH can be strongly coupled to conductive materials (carbon 49 nanotubes CNT, reduced graphene oxide rGO, etc.) with the 50 aim to make a highly conductive matrix with engineered het-51 erointerfaces capable of promoting fast charge transfer kinetics 52 during OER.^[8] 53

For this purpose, MXenes nitrides or carbides,^[9] have 54 recently attracted much attention because of their high elec-55 tronic conductivity (8000-10 000 S cm⁻¹).^[10] MXenes consist of 56 $M_{n+1}X_n$ octahedra layers (n = 1 to 3), which are obtained by the 57 exfoliation of the A element from $M_{n+1}AX_n$ precursors, a family 58 of 70+ known ternary carbides and nitrides, the so-called MAX 59

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Scheme 1. Schematic view of the protocol followed to synthesize Co-LDH@Ti $_3C_2T_x$ material.

18 phases (M = transition metal, A: group III-A or IV-A elements, 19 X: C and/or N).^[11] Moreover, the surface of MXenes sheets is 20 covered with terminal groups (T = -OH, -O, and/or -F) chemi-21 cally bonded to the metal atoms. These different T terminal 22 groups of $M_{n+1}X_nT_x$ are formed during the exfoliation step 23 and their nature (OH/O/F ratio) depends on the exfoliation environment.^[12] They can also act as anchoring points for nano-24 25 structured active phase, thus enabling a high dispersion degree 26 of nanocatalysts. In addition, the electron density on the catalyst surface atoms can be altered by the formation of MXene/ 27 active phase heterointerfaces, which is clearly of upmost impor-28 29 tance in the field of catalysis research.^[5a]

30 The wide range of possible substitutions in the M, X (core), 31 and T (surface) sites of MXenes leads to a large family of 2D $M_{n+1}X_nT_x$ materials with tunable properties opening an 32 immense, and largely unexplored, field of potential applica-33 34 tions. Among them, $Ti_3C_2T_r$ is the most studied material and 35 several works using it as support of electrocatalyst for OER such as C₃N₄,^[13] MOF,^[14] NiCoS,^[15] CoP,^[16] Co/N-CNT,^[17] 36 cobalt borate,^[18] FeOOH quantum dots,^[19] black phosphorus 37 quantum dots,^[20] and FeNi-LDH^[8b] have shown very promising 38 39 performances. Nevertheless, Ti₃C₂T_x MXene is prone to irreversible surface oxidation at ≈0.45 V versus Ag/AgCl,^[21] leading 40 to the formation of TiO₂ clusters. This strongly modifies its 41 surface electronic properties in strong alkaline media and at 42 43 electrode potentials required for the OER. As a consequence the stabilization of MXene in this potential range is a major chal-44 45 lenge. Unfortunately, in numerous reported studies on their use for oxygen electrocatalysis no information concerning the 46 surface chemical state of MXene under operating conditions 47 48 is provided and no special attention is paid to their potential 49 surface oxidation.

Herein, we report an innovative and quite simple polyol syn-50 51 thesis method enabling heterogeneous nucleation and growth 52 of cobalt layered double hydroxides Co-LDH on the surface of $Ti_3C_2T_x$ sheets without using the ZIF-67 chemical agent. 53 54 We show, for the first time that using this synthesis route, 55 the MXene surface state can be protected from oxidation. 56 Numerous physico-chemical characterization techniques were 57 employed in order to establish structural, morphological, and 58 electronic properties of the obtained composite material exhibiting promising catalytic properties for the OER in alkaline 59

media. Special attention was paid to the examination of interac-18 tion between Co-LDH and $Ti_3C_2T_x$ and to the surface chemical 19 state of the MXene substrate. It is shown that the heteroge-20 neous nucleation of Co-LDH phase results in the modification 21 of the Ti₃C₂T surface's electronic structure. This study consti-22 tutes therefore a major contribution as it paves the way for the 23 design of a new class of materials for OER involving a recently 24 discovered and very large family of 2D supports. 25

2. Results and Discussion

2.1. Composite Characterization

The facile synthesis route used to obtain Co-LDH@Ti₃C₂T_x 32 material is detailed in **Scheme 1**. It is a quite simple two-step 33 polyol process. After adsorption of reactants on MXene surface, the formation of Co-LDH phase at MXene surface occurs 35 consequently to a solvothermal treatment as described in the Experimental Section. 37

The XRI statterns of $Ti_3C_2T_x$, Co-LDH@Ti_3C_2T_x, and 38 Co-LDH, received with a Co K_α radiation source are reported 39 in **Figure 1**.

As evidenced by the absence of sharp diffraction peaks at 2θ 41 values of 11.1° and 22. 3° (see MAX XRD pattern-Figure S1 42 in the Supporting Information) in the diffraction pattern of the 43 $Ti_3C_2T_r$ sample (Figure 1a), the initial Ti_3AlC_2 MAX phase has 44 been fully converted into MXene. According to inductively cou-45 pled plasma optical emission spectroscopy (ICP-OES) analysis, 46 a very small amount of Al (lower than 0.05 Al per Ti₃C₂ unit) 47 remains in the sample, confirming Al etching. The *c* parameter 48 calculated for $Ti_3C_2T_x$ sample is of 22.6 Å, which is in good 49 agreement with values reported for samples prepared using 50 the LiF/HCl etching method and dried at 80 °C.^[12c] Shoulders 51 affecting the symmetry of 00l diffraction lines (e.g., (002) line 52 at $\approx 9^{\circ}$ or (004) line at $\approx 19.5^{\circ}$) can moreover be observed. These 53 can be ascribed to an interstratification phenomenon often 54 55 encountered on these claylike materials and indicating the coexistence of structures having different layer-to-layer distances.^[22] 56

The Co-LDH sample (Figure 1c) is composed of a mixture of 57 several phases: Co-LDH with characteristic peaks at 13.57° (003), 58 27.32° (006) 39.57° (010), 40.43° (012), 54.89° (0012), and 71.26° 59





Figure 1. XRD patterns of a) Ti₃C₂T_x, b) Co-LDH@Ti₃C₂T_x, and c) Co-LDH. All diffractograms were recorded with a Co K_{α} radiation source to limit fluorescence.

25 (110) (close to the JCPDS file no-00-046-0605 of $Co_5(O_{9.48}H_{8.52})$ 26 NO3 layered double hydroxides), Co(OH)2 (JCPDS file no-00-27 030-0443), and CoOOH (JCPDS file no-01-073-0497). Taking 28 into account that no nitrates are used in our synthesis, the inter-29 calated anions between Co-LDH layers are acetate ions from the 30 cobalt precursor salt. This intercalation process does not sig-31 nificantly impact the interlayer spacing since the 00l reflection 32 peaks positions are close to those reported for Co₅(O_{9,48}H_{8,52}) 33 NO3 material. On the diffraction patterns recorded for 34 Co-LDH@Ti₃C₂T_r composite (Figure 1b), (00l) and (110) dif-35 fraction lines of the MXene phase are clearly observed indi-36 cating the good preservation of this oxidation-sensitive phase 37 during the composite synthesis by our newly developed polyol method. No diffraction lines typical of TiO₂ can be observed, 38 39 further confirming that bulk oxidation of MXene does not occur. However, a dramatic shift of the (002) peak toward lower 40 diffraction angles leading to a *c* parameter value of 29.7 Å can be 41 42 noted in comparison with the initial MXene phase (c = 22.6 Å). This shift is higher than the one observed for MXene obtained 43 using Li salts as etching agent and dried at ambient conditions 44 (around 24-25 Å)^[22] and can be explained by the insertion of 45 cobalt and water molecules between the MXene sheets. The 46 possibility to insert 3d transition metal cations such as Feⁿ⁺ or 47 48 Coⁿ⁺ between MXene sheets has already been demonstrated in our previous works.^[12c] At first sight, the diffraction pattern 49 50 given in Figure 1b does not give any clear evidence of the for-51 mation of a well-crystallized cobalt-based phase. In the 2O range 52 where no intense diffraction lines associated to the LDH phase 53 (i.e., at diffraction angles lower than 10°, between 15°, and 25° 54 and between 30° and 39°), diffraction lines corresponding to 55 MXene phase are sharper ((002), (006), and (0010) diffraction lines for example). Nevertheless, one can notice that some 56 57 reflection lines ascribed to the MXene phase ((004) and (008) 58 diffraction lines for example) are quite broad. This shows the 59 presence of an additional contribution superimposed to the



MXene diffraction lines, which could correspond to (003) and 1 (006) reflection lines of Co-LDH. Moreover the (110) reflec- 2 tion line (72°, Figure 1b) of the Co-LDH phase is also observed 3 in the diffraction pattern recorded for the composite material 4 while it is not the case for MXene sample, definitely attesting 5 to the presence of crystallized LDH in this sample. Contrarily 6 to the pattern recorded with unsupported Co-based material 7 (Figure 1c), Co(OH)₂ and CoOOH crystallized phases are not 8 observed in the composite suggesting that the MXene promotes 9 the formation of LDH. This is probably due to the presence of 10 terminal groups such as -F, -OH, and -O, which may favor the 11 nucleation of Co-LDH as already reported during the synthesis 12 of NiFe-LDH/MXene material.^[8b] 13

To confirm the formation of the Co-LDH phase with organic 14 counter ions, electron energy loss spectroscopy (EELS) as well 15 as energy filtered electron diffraction (EFED) were performed 16 on Co-LDH@Ti₃C₂T_x composite in a Co-rich region. Given that 17 Co-LDH material is highly beam sensitive,^[6c] great care was 18 taken to study its irradiation induced damages during transmis- 19 sion electron microscopy (TEM) observations. The evolution of 20 the sample morphostructural and electronic properties through 21 EFED and EELS were then examined upon electron beam irra-22 diation (see Figure S2 and associated comments in part II in 23 the Supporting Information). An identification of the phase 24 before irradiation (Figure 2a) was then attempted. 25

Focusing first on the EDP, two diffuse rings are visible 26 (Figure 2a): the interplanar distances calculated from these two 27 rings are 2.67 and 1.57 Å. The here-measured distances are in 28 good agreement with those reported for Co-LDH by Xu et al. 29 using a similar TEM analysis: $d_{012}^{\text{LDH}} = 2.69 \text{ Å and } d_{110}^{\text{LDH}} =$ 30 1.56 Å.^[6c] Moreover, they are in good agreement with the 31 $d_{012}^{\text{LDH}} = 2.60 \text{ Å and } d_{110}^{\text{LDH}} = 1.54 \text{ Å determined from XRD}$ 32 (Figure 1) confirming the formation of the Co-LDH phase. A 33 typical carbon K edge recorded in the Co-LDH phase is pre-34 sented in Figure 2b (bottom part). The shape of the C K-edge 35 strongly differs from that of the MXene (top part of Figure 2b). 36 In particular, the sharp peak at the edge onset (labeled A) is 37 consistent with molecular-like levels.^[23] It is thus reasonable to 38 assume that the here-evidenced molecular carbon corresponds 39 to the acetate counter-anions of the Co-LDH phase.

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The Ti and Co contents of Co-LDH@Ti₃C₂T_x composite were measured by inductively coupled plasma optical emis- 42 sion spectroscopy. A Co/Ti atomic ratio of 1.4 was obtained, 43 which is close to the target content (ratio of 1.2). The small 44 difference can be explained by the initial MXene phase, which 45 is not exactly Ti₃C₂(OH)₂ because of the probable presence of 46 water between the sheets and the mixture of different terminal 47 groups. Moreover, the decanted water after centrifugation is 48 uncolored indicating that all initial introduced Co ions remain 49 in the composite indicating high covering rate of the MXene by 50 Co-LDH. 51

Scanning electron microscope (SEM) micrographs presented in **Figure 3**a,b clearly show the typical 2D-like MXene 53 morphology of the $Ti_3C_2T_x$ initial material. Sheets are tightly 54 stacked as reported for MXene synthesized with the etching 55 method involving the use of metal salts such as LiF.^[12b,c] The 56 morphology of this kind of sample strongly differs from that of 57 MXenes obtained using HF as the etching agent. The reason 58 is that the harsh HF environment leads to more defects and 59





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17 **Figure 2.** a) TEM micrography, together with the corresponding diffraction pattern and associated intensity profile. b) Comparison between typical C 18 K-edges obtained on a reference $Ti_3C_2T_x$ flake and in the Co-LDH phase.

20 thus to well separated sheets. In contrast, the milder condi-21 tions associated to the LiF/HCl environments together with the 22 induced intercalation of cations (i.e., Li⁺ in the present case), 23 which stabilize water layers strengthen the cohesion between 24 the sheets leading to more uniform structures as explained in 25 ref. [12b] and [12c]. For Co-LDH@Ti₃C₂T_x at low magnification 26 (Figure 3c,d), MXene multilayers seem to be embedded into a 27 Co-LDH matrix composed of porous sphere-like agglomerates. At higher magnifications these individual spheres are com-28 posed of LDH nanosheets forming an interconnected porous 29 network (Figure 3e,f). This microstructure is similar to those 30 reported for other LDH phases.^[6c,8b] The presence and relative 31 uniform distribution at macroscopic scale of Ti (from MXene) 32 and Co (from Co-LDH) elements in the Co-LDH@Ti₃C₂T_x 33 34 composite is revealed by elemental mapping analysis (Figure 35 S3, Supporting Information) even if one cannot exclude the 36 presence of some Co-rich or Ti-rich areas.

37 The Raman spectra of the as-synthesized $Ti_3C_2T_x$ and Co-LDH@Ti₃C₂T_x composite are presented in Figure 4. For the 38 39 MXene as well as the composite material, the spectra recorded present all the bands consistent with known vibrational modes 40 of Ti₃C₂T_x.^[24] This shows once again the preservation of the 41 MXene during the composite synthesis. In addition, Raman 42 bands centered at \approx 458 and 518 cm⁻¹ were also observed and 43 match with the position of the vibrational modes reported for 44 pure Co-LDH^[6c] indicating again the Co-LDH formation from 45 our synthesis route. 46

The surface chemistry of the Co-LDH@Ti₃C₂T_x composite 47 48 was also investigated by XPS (Figure 5) by recording signals 49 associated to Co2p (Figure 5a), C1s (Figure 5c), and Ti2p 50 (Figure S4, Supporting Information) core level spectra. The 51 Co2p signal is quite similar to the one recorded with $Co(OH)_2$ 52 commercial powder (Figure 5b) attesting for the presence of 53 Co²⁺ in the Co-LDH phase. No clear identification of Co³⁺ can 54 be performed suggesting that Co-LDH contains a low amount 55 of Co³⁺ cations.

In the C1s spectral region (Figure 5c), two major contributions are observed, centered at \approx 287 and \approx 290 eV, and can be respectively ascribed to C=O and O-C=O groups providing direct evidence for the presence of acetate ions as interlayer anions in the LDH material. The Ti-C bond contribution to 20 the C1s signal for as-synthesized $Ti_3C_2T_r$ is centered at $\approx 282 \text{ eV}$ 21 (Figure 5d). This contribution can also be observed for the 22 composite but the magnitude of the signal is quite low. This 23 is explained by the low analysis depth of the XPS technique 24 (5 to 10 nm) and by the high coverage of the MXene phase with 25 Co-LDH, as shown in SEM images (Figure 3). This is further 26 confirmed by the very low global intensity of the Ti2p core level 27 spectrum obtained for the composite as compared to the spec-28 trum obtained for the $Ti_3C_2T_x$ MXene (Figure S4 and associ-29 ated comments in part IV in the Supporting Information). 30 Nevertheless, the presence of the different Ti2p contributions 31 of the MXene in the composite again indicates the preservation 32 of MXene surface state during the synthesis (see part IV in the 33 Supporting Information). 34

2.2. Interaction between Co-LDH and $Ti_3C_2T_x$ Phases

A key point in the design of an efficient composite for elec-39 trocatalysis is the synergy between the different building 40 blocks. This interaction, the characterization of which is 41 very challenging and thus rarely successfully achieved, has 42 been probed using an approach based on the combination of 43 TEM-EELS and density functional theory (DFT) calculations. 44 The results are presented in Figures 6, 7, and 8. Focusing 45 first on Figure 6, one can observe that, on average, the MXene 46 sheets keep their integrity when mixed with the nanoparticles 47 during the formation of composites. Depending on the local 48 Co-phase coverage, the stacking of the MXene sheets is more 49 or less disorganized evidencing an intimate mixing between 50 the MXene and Co-LDH electrocatalyst. As an illustration, 51 Figure 6a evidences a clean MXene sheet (so-called zone 1-a) 52 with sharp edges and homogeneous TEM contrast (confirmed 53 by the diffraction pattern given in Figure 6b) in close contact 54 with the fibrous Co-LDH (see zones 1b-green circles). In other 55 regions, as evidenced in Figure 6c (corresponding to zone 2), 56 the MXene stack is structurally more perturbed as revealed by 57 the inhomogeneous contrasts and a more irregular shape. The 58 corresponding diffraction pattern, presented in Figure 6d, is 59







characteristic of a more disturbed MXene stack evidenced by additional diffraction spots between the main ones. However, the EFED pattern reveals the absence of oxide on the sample, evidencing the chemical stability of the MXene despite the dis-order. The degree of disorder in the MXene stack is apparently closely related to the Co phase coverage, which is inhomogeneous at the nanoscale: increasing the cobalt deposition tends to perturb the MXene stack organization, most probably due to Co intercalation in between the MXene sheets as evidenced later by EELS.

The Co-LDH coverage induces a modification of the MXene's electronic structure as evidenced using EELS, and characteristic of the interaction between Co-LDH and MXene. As an illus-tration, Figure 7a-c shows the EELS spectra collected on the different zones discussed in Figure 6 and their comparison with data collected on reference $Ti_3C_2T_x$ flakes. The low loss spectra recorded on zones 1a and 2 (Figure 7a), characteristic of the excitation of the valence electron gas in the MXene stack, are typical of MXenes: both the positions and global shapes of



Figure 4. Raman spectra of $Ti_3C_2T_x$ and Co-LDH@Ti_3C_2T_x composite.



Figure 5. High resolution XPS spectra: Co 2p for a) Co-LDH@Ti₃C₂T_x and b) commercial Co(OH)₂ and C 1s for c) Co-LDH@Ti₃C₂T_x and d) Ti₃C₂T_x.

30 the bulk plasmon (labeled C), and Ti $M_{2,3}$ edge (labeled D and 31 E) are in agreement with the reference spectrum (top curve),^[25] 32 confirming the preservation of the MXene general integrity. 33 Very importantly, one can notice the structure F corresponding 34 to the Co $M_{2,3}$ edge attesting for the presence of Co on these 35 MXene sheets. This was confirmed by the recording of the Co 36 $L_{2,3}$ edge (not shown here) on each one of these zones.

The C-K and Ti $L_{2,3}$ edges (providing element-selective information) were also recorded in order to characterize the electronic structure and local order within the MXene sheets. The C-K edges recorded on the different zones are presented in Figure 7b. The spectra confirm the analysis of the low-loss region: the spectrum collected in zone 1a is quite similar to



Figure 6. a) Micrography evidencing the coexistence of a clean stack of Ti₃C₂T_x sheets labeled zone 1-a (see the corresponding EFEDP in b)) and the fibrous Co-LDH in zones 1-b. c) Micrography of zone 2 evidencing a more disturbed MXene stack due to higher Co coverage (see the corresponding EFEDP in d)).

the reference spectrum.^[26] All the peaks A to D are present at the same energy positions (including the shoulder B' of structure B) with rather similar relative intensities with the noticeable exception of structure A, which has a significantly lower intensity. Part of this structure A was shown from DFT calculations to result from the hybridization between the unoc-cupied C-p and surface Ti-d states in the Ti₃C₂T₂ system^[26] sug-gesting a modification of the surface chemistry of the MXene support during the deposition of Co-LDH phase. This point is herein confirmed by DFT calculations performed on various structural models with different surface chemistries.

For the here-presented calculations, a $2 \times 2 \times 1$ supercell 41 consisting of two MXene sheets was used with nominal composition $Ti_3C_2F_x$ (as evidenced by Magne et al.^[26] –F and –OH 43 terminated systems have very similar C-K edges). 44

Since this structural model generates four surfaces, four dif-ferent surface configurations were considered (see Figure 8a): one surface fully covered (4 F atoms in $2 \times 2 \times 1$ supercell-labeled F4 in Figure 8a), one surface completely uncovered (labeled F0 in Figure 8a), one surface covered with 3 F atoms (labeled F3 in Figure 8a), and the last one covered with 1F atom (labeled F1 in Figure 8a). The K-edges corresponding to the carbon atoms below each one of these surfaces have then been simulated and are given in Figure 8b. These calculations all evidence the high sensitivity of the peak A to the surface functionalization, most of the investigated defects resulting in the decrease of the structure A intensity as observed in the case of the Co-LDH@Ti₃C₂T_x composite. In addition, our cal-culations also show the almost complete insensitivity of the structures at higher energy (from B to D). The high energy www.advancedsciencenews.com

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ntensity (arb. Units)



Zone 2

270 280 290 300 310 320 330 340 350 460 470 480 490 Energy loss (eV) Energy loss (eV) Energy loss (eV) Figure 7. a) Low loss spectra recorded on the zones 1-a (red) and 2 (blue) of the figure. b) C-K and c) Ti L_{2.3} edges recorded on zones 1-a and 2. Black curves correspond to reference spectra obtained on a pure $Ti_3C_2T_x$ sample synthesized using the LiF/HCl etching method.

Zone 2

region is thus much more characteristic of the inner electronic structure of the MXene sheet in agreement with the analysis of Magne et al.^[26] These results suggest that although the MXene sheets have been preserved, their surface chemistry/electronic structure is modified upon functionalization with the Co nanoparticles. Very importantly, this effect is observed at the entire flake scale, evidencing the global coupling between the catalyst and its support. One can notice that in the spectrum recorded in zone 2 (Figure 7b), the structures B, C, and D are broadened evidencing a more pronounced effect on the electronic structure of the inner part of the MXene sheet. These data complement the corresponding EFEDP (Figure 7d) evidencing

probably more defects within the corresponding MXene sheets. It is important to notice that defects may play a positive role in the present composite serving as anchoring points for the cata-lyst dispersion. Another important point is that these defects do not alter the general valence band structure of the material as probed in the low loss region and discussed before (see the low 29 loss spectra in Figure 7a).

Zone 2

To complete the EELS analysis, titanium edges were 31 recorded. The Ti L_{2,3} edge of zone 1 on Figure 7c) is charac-teristic of Ti₃C₂T_x. Hence, in agreement with the EFDP, spec-troscopy (LL, C-K, and Ti L_{2.3} edges) confirms that the inner structure of the $Ti_3C_2T_x$ sheets is preserved. The Ti $L_{2,3}$ edge







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14Figure 9. a) Voltammograms recorded in a nitrogen-saturated 1 mol L⁻¹ KOH electrolyte with $Ti_3C_2T_x$ sample (inset graph) and with Co-LDH@Ti_3C_2T_x1415catalyst. Scan rate 50 mV s⁻¹. b) Linear sweep voltammograms recorded in a nitrogen-saturated 1 mol L⁻¹ KOH electrolyte with $Ti_3C_2T_x$ sample, Co-LDH1516Co-LDH@Ti_3C_2T_x, Co-LDH + Ti_3C_2T_x and commercial IrO2 catalysts using a rotating disk electrode set at 1600 rpm. Co-LDH + Ti_3C_2T_x refers to a sample1617resulting from the mechanical mixing of Co-LDH and $Ti_3C_2T_x$ materials. Scan rate 5 mV s⁻¹.171818

19 acquired on zone 2 present a slight splitting of both the L_3 and 20 L_2 edges (labeled A' and B' respectively), which indicate a modi-21 fication of the electronic structure of the material. As already 22 mentioned, this is supported by the broadening of structure B, 23 C, and D at the C-K edge. However, the structure of the MXene 24 is conserved according to diffraction and these modifications 25 do not result from the oxidation of the sheets.

26 From this analysis, it turns out that the covering of the MXene with the cobalt phase results in the conservation of 27 28 the structure of the material and in a strong coupling between 29 the Co-LDH catalyst and the MXene support as revealed by EELS. We propose these electronic structure modifications to 30 31 be characteristic of the synergistic effect between the MXene and Co-LDH phase explaining the high electrocatalytic perfor-32 mances of this composite as described in the next section. 33

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36 2.3. Electrochemical Performances

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38 The electrochemical behavior of Co-LDH@Ti₃C₂T_x and Ti₃C₂T_x 39 materials was first characterized in a nitrogen-saturated 40 1 mol L⁻¹ KOH electrolyte using a scan rate of 50 mV s⁻¹. The 41 resulting cyclic voltammograms are presented in **Figure 9**a.

For the $Ti_3C_2T_x$ sample, an irreversible oxidation peak 42 centered at ≈ 0.92 V versus RH positive going scan of the first voltametric cycle. In the absence 43 44 45 of redox active species in the electrolyte, this redox peak is assigned to the oxidation of the $Ti_3C_2T_x$ material and especially 46 to the oxidation of Ti atoms.^[19] After the first voltammetric 47 cycle, no further surface oxidation can be observed during 48 49 the second cycle as evidenced by the disappearance of the 50 irreversible oxidation peak centered at 0.92 V (inset graph of 51 Figure 9a and Figure S5, Supporting Information). This shows 52 that the surface of $Ti_3C_2T_x$ is then fully oxidized. The deposition of the Co-LDH phase onto the MXene surface appears to 53 54 prevent the surface oxidation of the MXene as evidenced by 55 the disappearance of the irreversible oxidation peak during the first voltammetric cycle recorded for the composite mate-56 57 rial (Figure 9a). Taking into account results obtained from 58 physico-chemical characterization of Co-LDH@Ti₃C₂T_x composite showing that surface chemistry of $Ti_3C_2T_x$ is preserved 59

consequently to Co-LDH deposition, it can be deduced that 19 Co-LDH phase acts as a protective layer against MXene oxida-20 tion and makes possible the presence of nonoxidized MXenes 21 at electrode potentials required for the OER. This is of upmost 22 importance in order to preserve a high electronic conductivity 23 and decrease the charge transfer resistance at the interface 24 between Co-LDH and $Ti_3C_2T_x$. This constitutes a major result 25 of the present study. 26

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Taking into account thermodynamic data provided by Meier 27 et al,^[27] one can assume that the large oxidation peak centered 28 at ≈ 1.2 V versus RHE for the composite electrode during the 29 positive scan can be ascribed to Co^{2+}/Co^{3+} redox transition. 30 At higher potentials (i.e., higher than 1.3 V vs RHE), Co3+ 31 containing surface species are oxidized into Co4+ giving rise 32 to the formation of active sites for OER.^[4] The electroactivity 33 of the as-prepared composite toward OER was evaluated by 34 recording linear sweep voltammograms in a nitrogen-saturated 35 1 mol L^{-1} KOH electrolyte at a scan rate of 5 mV s⁻¹ and using 36 a rotating disk electrode set at a rotating rate of 1600 rpm. 37 The ohmic drop corrected curves presented in Figure 9b first 38 indicate the high activity of Co-LDH@Ti₃C₂T_x composite 39 catalyst toward OER since the electrode potential required to 40 drive a current density of 10 mA cm⁻² (E_{i10}) is only of 1.57 V 41 versus RHE and much lower than the one obtained for unsup-42 ported Co-LDH (1.62 V vs RHE). This underlines the posi-43 tive role played by the intimate contact between $Ti_3C_2T_x$ and 44 Co-LDH. Note that the amount of Co species, considered as 45 active nanocatalysts, is lower in the composite. Performances 46 of Co-LDH+Ti₃C₂T_x sample resulting from the mechanical 47 mixing of Co-LDH and $Ti_3C_2T_x$ powders are also lower than for 48 Co-LDH@Ti₃C₂T_r material. This can be either due to a higher 49 charge transfer resistance resulting from the low intimacy of 50 the contact between both phases and to the low phase purity 51 of supportless synthesized Co-LDH material as discussed in 52 the manuscript (Figure 1c). The lower activity of the mixture 53 in comparison with Co-LDH alone can be explained by a lower 54 amount of active site (amount of cobalt). Furthermore the 55 electrochemical performance obtained herein with Co-LDH@ 56 $Ti_3C_2T_x$ composite catalyst are better than those obtained 57 with the IrO₂ commercial catalyst ($E_{i10} = 1.64$ V vs RHE) and 58 of the same order of magnitude as those reported for other 59



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1 MXene-supported LDH materials (see Table S1 in the Sup-2 porting Information) with an easier synthesis route allowing 3 preserving the MXene surface state. The Tafel slope values 4 obtained are another parameter confirming the high efficiency 5 of the Co-LDH@Ti₃C₂T_x composite catalyst toward OER. This 6 latter catalyst indeed exhibits a Tafel slope of 82 mV dec⁻¹ 7 whereas it is of 98 mV dec-1 for the unsupported Co-LDH 8 material. Finally as shown in Figure S6 (Supporting Informa-9 tion), this catalyst is capable of delivering a constant operating 10 potential value of 1.52 and 1.56 V versus RHE for 20 h when 11 galvanostatically biased at 5 and 10 mA cm⁻², respectively.

¹⁴ **3. Conclusion**

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In summary, a new and simple polyol method is here proposed 16 17 for the synthesis of Co-LDH@MXene composite showing high performances for oxygen evolution reaction. The presence of 18 19 the layered MXene favors the growth of this Co-based structure, 20 highly active for the studied reaction. The presence of terminal 21 groups on the MXene structure allows a good dispersion of the active phase. By this way, the MXene structure can be pre-22 23 served from oxidation during the composite synthesis as well 24 as under high potential during the electrochemical analyses 25 by total recovery of its surface with the cobaltite phase. This 26 constitutes a major result of this study and, more generally, for applications involving MXenes as support (batteries, superca-27 28 pacitors, etc.). Indeed, the preservation of the MXene structure 29 is crucial to maintain high electrical conductivity, a key factor to perform efficient electrodes for metal-air batteries or water 30 31 electrolyzers. It has also been shown by EELS in an original way that high interaction appears between Co-LDH and the MXene 32 with the modification of the MXene surface electronic struc-33 34 ture, probably thanks to the presence of terminal groups on the 35 MXene surface. This interaction is a key element allowing to 36 improve the electrochemical performances in comparison with the cobaltite phase alone through a synergistic effect. 37

Considering the simplicity of the synthesis method and the possibility to easily tune both the nature of the active phase and the MXene composition, there is little doubt that there is room for major improvements in the near future for the design of much more efficient MXene-based oxygen electrocatalysts with major impact for energy storage and conversion applications.

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46 **4. Experimental Section**

47 Synthesis of $Ti_3C_2T_x$: The synthesis of $Ti_3C_2T_x$ materials is based on 48 the previous work.^[12b] 1 g of LiF (Aldrich) were added to 20 mL of HCl 49 6 mol L⁻¹, prepared from HCl 37% (Sigma-Aldrich) and stirred during 50 0.5 h. Then, 1 g of Ti_3AlC_2 (see part I in the Supporting Information 51 for the MAX synthesis) with initial particle size lower than 25 µm 52 obtained after sieving, were progressively introduced in the solution to avoid initial overheating. The mixture was heated at 60 °C for 72 h 53 and maintained under magnetic stirring. Then, the suspension was 54 washed and centrifuged 4 times with water at 6000 rpm for 6 min, the 55 supernatant liquid being decanted each time. The sediment was filtered 56 using a vacuum-assisted filtration device (PVDF membrane, 0.22 μ m 57 pore size) and dried overnight at 80 °C.

58 Synthesis of Co-LDH@ $Ti_3C_2T_x$ and Co-LDH: In order to synthesize 59 the Co-LDH@ $Ti_3C_2T_x$ composite, 190 mg of $Ti_3C_2T_x$ powder was dispersed first in 196 mL of ethylene glycol (99.8%, Sigma Aldrich) 1 with an ultrasound bath for 10 min under argon, Ar, atmosphere to 2 delaminate the MXene sheets. Then, 570 mg of anhydrous cobalt (II) 3 acetate (98+%, Alfa Aesar) was added to this suspension. After 0.5 h, 4 130 mg of NaOH (≥97%, Aldrich) were added and the mixture was 5 stirred under Ar overnight at room temperature, RT. Then, the solution 6 was transferred into a sealed autoclave before being heated at 200 °C 7 for 3 h under N₂ flow. The final product was centrifuged at 9000 rpm for 15 min after being dispersed in ethanol (1st washing) and deionized 8 water (2nd washing). The supernatant liquid was decanted and the 9 sediment was filtered, washed with deionized water and dried overnight 10 at RT. Assuming the initial composition of the MXene is $Ti_3C_2(OH)_2$, the 11 amount of each precursor was selected to obtain a final ratio of 3.6 cobalt 12 atom per $Ti_3C_2(OH)_2$ unit corresponding to a Co/Ti atomic ratio of 1.2. 13 The amount of Co was chosen to obtain a high coverage of the MXene.

The sample labeled Co-LDH was produced in the same way, but 14 without the addition of MXene powder. 15

Material Characterization:The morphology of the synthesized10composite was characterized using a field emission gun scanning16electron microscope (FEG-SEM) 7900F from JEOL. This microscope17is equipped with an energy dispersive X-ray spectrometer (EDS) from18Brücker (with Esprit software) allowing the mapping of the Ti and Co19elements.20

XRD patterns were recorded using PANalytical EMPYREAN powder diffractometer using Co K_{α} radiation source ($\lambda = 0.1789$ nm) in order to limit fluorescence phenomenon. Diffractograms were collected between 5° and 80° applying a step size of 0.066° and a step time of 420 s.

The composites were also examined by Raman spectroscopy. These24experiments were carried out using a HORIBA Jobin Yvon HR80025confocal Raman microscope with a CCD detector. Spectra were acquired26at RT using an excitation wavelength of 632.8 nm.27

The Al, Ti, and Co contents of the composite were determined 28 by inductively coupled plasma-optical emission spectrometry using 29 a PerkinElmer Optima 2000DV instrument at a base pressure of 30×10^{-8} Pa.

31 The XPS analysis were carried out with a Kratos Axis Ultra DLD 32 spectrometer using a monochromatic Al K_{α} source (1486 eV, 10 mA, 15 kV). When required, a charge neutralizer system was operated for 33 the analysis. Instrument base pressure was 9×10^{-8} Pa. High-resolution 34 spectra were recorded using an analysis area of 300 μ m \times 700 μ m² 35 and a 20 eV pass energy. These pass energies correspond to Ag $3d_{5/2}$ 36 FWHM of 0.55 eV. Data were acquired with 0.1 eV steps. All the binding 37 energies were calibrated with the C1s (C-Ti-T_x) binding energy fixed at 282 eV as an internal reference. 38

Transmission electron microscopy experiments were performed on 39 reference $Ti_3C_2T_x$ samples as well as on the Co-LDH@ $Ti_3C_2T_x$ composites 40 obtained using the polyol method. Samples were characterized using 41 electron energy loss spectroscopy and energy filtered electron diffraction 42 in order to check the MXene structure both at the short range level 43 (fine structure at core edges in EELS being sensitive to the local order 44 on a $\approx 6-7$ Å scale around the excited atom^[28]) and long range level. In addition, TEM-EELS and EFED were also used to characterize the 45 nature of the obtained Co active phase. Experiments were performed in 46 a JEOL 2200 FS microscope equipped with an in-column omega filter. 47 The operating voltage of the TEM was 200 kV, the energy resolution in 48 EELS was about 1.0 eV and the collection angle was fixed to 7 mRad. 49 EEL spectra were recorded in the core-loss region, giving access to the 50 electronic structure (the unoccupied p-states for K edges) projected on the excited atoms, and in the low-loss region which corresponds to the 51 excitation of valence electrons. Core-loss spectra were extracted from the 52 background using a power law and the multiple scattering was removed 53 using the well-known Fourier-ratio method.^[29] EFED patterns (EFEDP) 54 were acquired using a 10 eV slit and analyzed using the software 55 JEMS.^[30] The TEM samples were prepared by dispersing the composite 56 powders on the inner surface of a beaker and then picking them up on a 57 TEM copper grid covered with lacy carbon film.

Density Functional Theory Calculations: The energy loss near edge 58 structure (ELNES) at the C K-edge and its connection to the surface 59



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functionalization of the MXene is interpreted by comparison with simulations based on the density functional theory, DFT, and performed 2 with the WIEN2K code.^[31] WIEN2k is an all-electron code using the 3 full-potential augmented plane wave plus local orbitals method to 4 solve the Kohn-Sham equations. Calculations were performed in the 5 generalized gradient approximation using the PBE exchange-correlation 6 functional,^[32] which has been shown to give a good description of EEL 7 spectra in Ti₃C₂T_r.^[25,26]

8 Given that simulations performed on $Ti_3C_2F_2$ and $Ti_3C_2(OH)_2$ were shown to give similar ELNES at the C K-edge,^[26] the here-9 presented calculations were performed on a Ti₃C₂F_x system described 10 using a 2 \times 2 \times 1 supercell (P3m1 space group, a = b = 6.1168 Å and 11 c = 19.58826 Å) in order to take the core-hole into account and allow for 12 different functionalizations of the MXene sheets as discussed in the text. 13 Atomic sphere (muffin-tin) radii of 1.73, 2.09, and 1.99 a.u. were used for carbon, titanium, and fluoride atoms respectively. The product of the 14 lowest muffin-tin radius with the highest wave vector used in the plane 15 wave expansion RK_{max} was converged at 8.0. The first Brillouin zone 16 integration was converged for 1500 k-points for the SCF calculation. 17

The EELS spectra were obtained from the band structure using the 18 Telnes3 extension of WIEN2k: it allows for the calculation of the electron 19 inelastic scattering cross-section in a relativistic approach, a very 20 important consideration for anisotropic materials.^[33]

Electrochemical Measurements: All electrochemical measurements 21 were carried out at RT in a standard three-electrode electrochemical cell 22 using potentiostat Autolab (PGSTAT-302N) coupled with a rotating disc 23 electrode (RDE). An Ag/AgCl (saturated KCl-filled) ($E_{AgCl/Ag} = 1.02$ V vs 24 ERH) electrode and a glassy carbon plate were used, respectively, as a 25 reference and counter electrodes. A 3 mm diameter glassy carbon (GC) 26 disc was used as the working electrode substrate. The catalytic inks were 27 prepared by dispersing 9 mg of catalyst powder in a mixture composed of ultra-pure water (500 μ L), isopropanol (500 μ L), and Nafion (100 μ L), 28 followed by ultrasonication for 10 min. 3 μ L of the dispersed catalyst 29 were deposited onto the surface of the working electrode (catalyst 30 loading of 0.35 mg cm⁻²) and the deposit was dried under N_2 flow.

31 The measurements were conducted in a N₂ saturated 1 mol L^{-1} 32 KOH (86.5%, VWR) aqueous electrolyte. First, cyclic voltammograms were recorded in a nitrogen-saturated electrolyte from 0.15 to 1.35 V 33 versus RHE at a scan rate of 50 mV s⁻¹. Then the activity of catalysts 34 toward OER was examined by recording linear sweep voltammograms 35 from 0.95 to 1.75 V versus RHE at a scan rate of 5 mV s^{-1} by applying 36 a rotating rate of 1600 rpm to the RDE. All measurements were IR-drop 37 corrected by determining the cell resistance using electrochemical 38 impedance spectroscopy measurements (EIS) between 0.1 Hz-100 KHz. Spectra were acquired in the capacitive region with a Solartron SI 39 1287 electrochemical interface and an SI 1260 impedance/gain-phase 40 analvzer. 41

These electrochemical measurements were conducted on Co-LDH@ 42 Ti₃C₂T_x, Co-LDH, and commercial IrO₂ (99.9%, Alfa Aesar). 43

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Supporting Information 46

47 Supporting Information is available from the Wiley Online Library or 48 from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

11 layered double hydroxide (LDH), MXenes, oxygen evolution reaction, 12 polyol synthesis 13

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