Au–Manganese Oxide Nanostructures by a Plasma-Assisted Process as Electrocatalysts for Oxygen Evolution: A Chemico-Physical Investigation

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1. Introduction

The design and development of cost-effective, durable and highly active electrode materials for the oxygen evolution reaction (OER) is a critical issue towards commercially viable solutions for electrochemical water splitting, CO2 reduction, regenerative low-temperature fuel cells, and rechargeable metal-air batteries.[1–6] In particular, the first kind of process has received a considerable attention for the generation of hydrogen, a strategically attractive energy vector, from water, an abundant natural resource, with no release of toxic/harmful byproducts and in full compliance with the most stringent environmental requirements.[7–13] Nevertheless, OER imposes a large overpotential due to its inherently sluggish kinetics, related, in turn, to the energy demanding multiple bond rearrangements and the associated complex multielectron transfer steps.[4,8,12,14–17] Up to date, few catalysts have provided OER electrocatalytic activities and low overpotentials.

Earth-abundant and eco-friendly manganese oxides are promising platforms for the oxygen evolution reaction (OER) in water electrolysis. Herein, a versatile and potentially scalable route to gold-decorated manganese oxide-based OER electrocatalysts is reported. In particular, Mn_xO_y (MnO_2, Mn_2O_3) host matrices are grown on conductive glasses by plasma assisted-chemical vapor deposition (PA-CVD), and subsequently functionalized with gold nanoparticles (guest) as OER activators by radio frequency (RF)-sputtering. The final selective obtainment of MnO_2- or Mn_2O_3-based systems is then enabled by annealing under oxidizing or inert atmosphere, respectively. A detailed material characterization evidences the formation of high-purity Mn_xO_y dendritic nanostructures with an open morphology and an efficient guest dispersion into the host matrices. The tailoring of Mn_xO_y phase composition and host–guest interactions has a remarkable influence on OER activity yielding, for the best performing Au/Mn_2O_3 system, a current density of \(\approx 5\) mA cm\(^{-2}\) at 1.65 V versus the reversible hydrogen electrode (RHE) and an overpotential close to 300 mV at 1 mA cm\(^{-2}\). Such results, comparing favorably with literature data on manganese oxide-based materials, highlight the importance of compositional control, as well as of surface and interface engineering, to develop low-cost and efficient anode nanocatalysts for water splitting applications.

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viable for practical applications, and most of them are based on metals/metal oxides containing rare, expensive, and toxic elements, such as Ru and Ir.[2,7,9,17,19] As a consequence, there is an open demand for novel non-noble metal oxides combining optimal catalytic performances with low cost and high durability.[3,8,13,14,20] Among the possible alternatives, manganese oxides (MnOx) and, in particular, MnO2 and Mn2O3, come to the fore thanks to their low toxicity, large natural abundance, and rich redox chemistry.[4,5,8,9,13,18,21,24] So far, MnOx-based OER catalysts have demonstrated a good structural stability and encouraging performances in alkaline media,[1–3,6,11] although the exact role of MnOx phase composition, as well as of surface and defect chemistry, undoubtedly require further investigation.[4,6,13,18,25]

So far, various strategies have been proposed and applied to tailor MnOx-based material chemico-physical properties and functional performances for the target applications.[7,9,21,26] In this regard, an amenable approach involves the controlled fabrication of multicomponent systems, which offer additional degrees of freedom with respect to their single-phase counterparts.[1,3,14,17,22] In this scenario, functionalization with Au nanoparticles (NPs) even in trace amounts has proved to be effective in enhancing oxygen evolution performances, due to local interactions at Au/MnOx neighboring sites.[1,3,8] In particular, the occurrence of a strong metal-support interaction (SMSI) at the Au/MnOx interface involves a charge redistribution between guest metal and host support.[2,21,27,28] This phenomenon, in turn, involves the formation of oxygen vacancies on manganese oxide at the interface with Au NPs.[29–32] Overall, the control of the aforementioned effects through a controllable material design and processing is of outstanding importance to achieve enhanced OER performances.

In the present study, MnOy (MnO2, Mn2O3) nanomaterials (host) are grown on fluorine-doped tin oxide (FTO) substrates by plasma assisted-chemical vapor deposition (PA-CVD), functionalized with gold NPs (guest) by radio frequency (RF)-sputtering under mild conditions, and subjected to ex situ thermal treatment (Scheme 1). The advantages of the proposed synthetic approach are: (i) the direct obtainment of supported, mechanically stable materials, avoiding typical drawbacks of the homologous powdered ones (e.g., the need for postsynthesis immobilization procedures);[5,7,11,13,18,33] (ii) the possibility of selectively directing the host matrix evolution to Mn(IV) or Mn(III) oxide starting from the same manganese oxide deposits, as a function of the annealing atmosphere (air or Ar, respectively);[38,26] (iii) the obtainment of a tailored Au NP dispersion, as well as of an intimate host–guest contact;[34,35] (iv) the introduction of oxygen vacancies during the PA-CVD, RF-sputtering, and annealing steps.[26,30,36]

The advantages offered by the adopted preparation route provide a versatile toolkit for the mastering of material characteristics. In this work, interrelations between preparative conditions, chemico-physical properties and OER functional behavior of the developed MnOx-based materials are presented and critically discussed, proposing also a possible mechanism accounting for the improved performances achieved upon gold functionalization.

2. Results and Discussion

MnO2- and Mn2O3-based samples were grown on FTO-coated glass supports according to the synthetic approach shown in Scheme 1 (see the Experimental Section for further details). Due to the strongly oxidizing character of oxygen-containing plasmas, related, in turn, to the presence of a high number of reactive O-containing species (O2+, O+, O, …),[37] the direct growth of phase-pure MnOx systems via PA-CVD (step 1 in Scheme 1) turned out to be unfeasible. In fact, the above species induce a significant oxidation of Mn(II) centers contained in the precursor molecules, and for temperatures between 200 and 300 °C the Mn–O deposit obtained in the first PA-CVD step comprises β-MnO2 (pyrolusite) as the sole crystalline phase, irrespective of the Ar/O2 content and of the deposition substrate.[33–35,38,39] For higher growth temperatures, earlier data indicated a partial MnO2 thermal decomposition to Mn2O3,[31] but the latter could not be obtained in its pure form. On the other hand, PA-CVD from the same manganese precursor and oxygen-free (pure Ar) plasmas yielded the formation of MnF2 rather than manganese oxides.[38] As a consequence, basing on previously reported results,[38] annealing of the obtained systems (step 3 in Scheme 1) was performed in air or in Ar to yield MnO2- or Mn2O3-based materials, respectively. In both cases, thermal treatments were performed after Au introduction (step 2 in Scheme 1), in order to stabilize the obtained systems prior to functional tests.

For air-annealed samples, X-ray diffraction (XRD) analyses (Figure 1a) revealed, beside FTO substrate reflections, two
signals at $2\theta = 28.7^\circ$ and $37.3^\circ$, that could be indexed to the (110) and (101) crystalline planes of $\beta$-MnO$_2$ \cite{35,38,40} (mean crystallite size $20 \pm 2$ nm). In a different way, for specimens subjected to thermal treatment under Ar, the diffraction peaks at $2\theta = 23.2^\circ$, $33.1^\circ$, and $38.3^\circ$ well matched with the (211), (222), and (400) reflections of $\beta$-Mn$_2$O$_3$ (bixbyite) \cite{15,41} (average crystallite dimensions $= 45 \pm 5$ nm). The relatively weak and broad Mn$_x$O$_y$ (MnO$_2$, Mn$_2$O$_3$) signals indicated a high material defectivity,\cite{33,35} as further discussed below. The absence of reflections from metallic Au was traced back to the relatively low content and high dispersion of gold particles.\cite{2,34}

X-ray photoelectron spectroscopy (XPS) analyses were run to investigate the surface composition of the synthesized materials. As can be observed from Figure 1b, the main Au photoelectron peaks could be clearly discerned in the wide-scan spectra of gold-decorated samples. Nonetheless, such specimens clearly revealed the manganese and oxygen signals detected also on the corresponding gold-free samples. Taking into account the surface sensitivity of the XPS technique, these results suggest an effective dispersion of Au nanoparticles on Mn$_x$O$_y$ (MnO$_2$, Mn$_2$O$_3$) and the formation of a high density of Au/Mn$_x$O$_y$ junctions, a favorable issue in view of electrocatalytic applications.\cite{34,39}

In agreement with the above XRD results, the high resolution Mn2p and Mn3s XPS signals (Figure 2a,b, respectively) confirmed the obtainment of pure MnO$_2$- and Mn$_2$O$_3$-based materials for both bare and gold-decorated Mn$_x$O$_y$ systems. In fact, for air-annealed samples, the Mn2p XPS spectrum showed two spin-orbit components at binding energies (BE) of $642.5 \pm 0.2$ and $654.1 \pm 0.2$ eV corresponding to Mn2p$_{3/2}$ and Mn2p$_{1/2}$, respectively, in line with literature data for manganese (IV) oxide.\cite{33,38,42,43} This conclusion was further confirmed by the BE difference between the Mn2p$_{3/2}$ peak and the O1s lattice component (I, see below) of $112.7 \pm 0.2$ eV,\cite{34,35} as well as by the Mn3s multiplet splitting separation of $4.7 \pm 0.2$ eV.\cite{10,38,39} As far as specimens annealed in Ar are concerned, the Mn2p$_{3/2}$

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**Figure 1.** a) XRD patterns and b) XPS survey spectra of bare and gold-decorated Mn$_x$O$_y$ (MnO$_2$, Mn$_2$O$_3$) samples.
and Mn2p3/2 component BEs shifted to 641.8 ± 0.2 and 653.5 ± 0.2 eV. In addition, the Mn2p3/2-O1s BE difference and the Mn3s multiplet splitting separation were 111.6 ± 0.2 and 5.3 ± 0.2 eV, respectively. As a whole, these results support the obtainment of manganese(III) oxide.

For all samples, two components contributed to the O1s signal (Figure 2c). The main one, located at BE = 529.9 ± 0.2 eV (I), was ascribed to Mn–O–Mn bonds, whereas a second one at 531.8 ± 0.2 eV (II) was attributed to –OH groups chemisorbed on oxygen vacancies. Interestingly, the contribution of the latter component to the whole O1s signal increased by ≈10 % on going from bare MnₓOᵧ (MnO₂, Mn₂O₃) systems to the corresponding gold-decorated ones, indicating a higher concentration of oxygen defects on Au/MnO₂ and Au/Mn₂O₃ specimens. This phenomenon likely arises from two concomitant effects taking place during the sputtering step (see Scheme 1): (i) the bombardment of MnₓOᵧ surface;[30,36] (ii) the occurrence of a SMSI effect at the Au/MnₓOᵧ interface (see below for further details), involving the formation of additional oxygen vacancies following a host–guest charge redistribution.[27,29–32]

The Au4f7/2 and Au4f5/2 spin-orbit components (Figure 2d) were located at 84.5 ± 0.2 and 88.1 ± 0.2 eV, respectively. Such values, ≈0.5 eV higher that those typically reported for Au(0),[43] suggested an appreciable electron transfer from gold NPs to MnₓOᵧ at the metal/oxide interface, in line with the above mentioned SMSI effect.[29–32,39,45] This phenomenon, reasonably enhanced by the efficient dispersion of gold nanoparticles in MnₓOᵧ nanostructures (as indicated by secondary ion mass spectrometry (SIMS) results, see below and Figure 3), is expected to play a beneficial influence on the OER electrocatalytic behavior of the developed systems.[29,32,45] Quantitative analyses (see also§ S.1 and Figure S1 in the Supporting Information) yielded an Au/Mn atomic ratio of 0.20 ± 0.01 for both Au/MnO₂ and Au/Mn₂O₃ specimens, indicating a comparable surface coverage of the host matrices by Au NPs.

SIMS analyses were subsequently undertaken to probe the system in-depth composition and obtain complementary information with respect to XPS ones. Irrespective of preparative conditions, SIMS profiles (Figure 3) clearly revealed a nearly parallel trend for manganese and oxygen yields from the surface down to the deposit/substrate interface, in line with the uniform formation of single-phase MnO₂ or Mn₂O₃ throughout the sample thickness. The relatively slow rise of tin signal was mainly related to the appreciable FTO roughness, as also

![Figure 2. Surface a) Mn2p, b) Mn3s, c) O1s, and d) Au4f XPS signals for bare and gold-decorated MnₓOᵧ (MnO₂, Mn₂O₃) samples. Color codes as in panel (a).](image-url)
evidenced by field emission-scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images (see below). Interestingly, at variance with Mn and O trends, the Au ionic yield progressively decreased within the deposit, down to a depth value of ≈250 nm. This result indicated that, despite gold was preferentially concentrated close to the MnO2 surface, it was also dispersed in the inner host matrix regions. Such a phenomenon, in line with previous results on composite nanomaterials obtained by combined PA-CVD + RF-Sputtering preparation routes,[34,35] can be traced back to the synergy between the porous MnO2 morphology, characterized by the presence of voids (see below), and the inherent RF-sputtering infiltration power (see Scheme 1). The combination of these features is responsible for gold introduction even in the inner manganese oxide regions, accounting thus for the trends of Au SIMS profiles in Figure 3b–d.

Optical absorption spectra of bare MnO2 samples and gold-decorated ones are reported in Figure 4. All samples showed a progressively increasing absorption at lower wavelengths, that turned out to be steeper below 800 nm in line with the occurrence of MnOx interband electronic transitions. Tauc plots analysis (see insets in Figure 4a,b) yielded band gap ($E_G$) values of 2.00 ± 0.05 and 2.15 ± 0.05 eV for MnO2- and Mn2O3-based materials, respectively, in good agreement with previous literature data.[10,22,33] The absorption tail extending towards the near-infrared region was attributed to the presence of oxygen vacancies promoting the formation of sub-band gap states.[33,46] The sub-bandgap absorption tailing was present even for gold-free samples, suggesting an appreciable concentration of oxygen vacancies even in bare MnO2 and Mn2O3. This effect can favorably influence the system electrocatalytic performances[7,13,47,48] (see also below).

In line with the above XPS results, showing an increased O defect content for Au-decorated samples, the spectra in Figure 4 revealed an enhanced light absorption for Au/MnO2 and Au/Mn2O3 specimens in comparison to the homologous bare manganese oxides, and a slight $E_G$ decrease of ≈0.1 eV upon gold sputtering.[39,47,48]

The system morphology and nanoscale structure were investigated through the combined use of FE-SEM, atomic force microscopy (AFM) and TEM analyses. An overview of plane-view and cross-sectional FE-SEM images for all samples is given in Figure S2 in the Supporting Information. Irrespective of preparative conditions, specimens were formed by elongated

![Figure 3. SIMS depth profiles of bare and gold-decorated MnO2 (MnO2, Mn2O3) samples.](image-url)
Subsequently, special attention was devoted to the thorough analysis of gold-containing samples by TEM and energy dispersive X-ray spectroscopy (EDXS). To this aim, Figure 5b–d provides a detailed insight into the structural and compositional features of the Au/Mn$_2$O$_3$ specimen (see Figure 5a). Figure 5b displays a representative cross-sectional bright field TEM image, which evidenced the formation of dendritic branched structures. The latter were found to outgrow from the zig–zag shape faceted surface of the underlying FTO substrate, giving rise to irregular nanodeposits with an open morphology. The typical lateral size of manganese oxide dendrites was 120 ± 20 nm (Figure 5b–d). Such nanostructures, whose formation takes place at higher growth rates under a diffusion-controlled kinetic regime,[49–51] are highly desirable for the target applications thanks to the low branch radial size and high material/electrolyte contact area, which, in turn, reduce charge carrier diffusion distances and favorably affect interfacial reactions.[52]

Indeed, the numerous lateral trunk/branch junctions provide a direct pathway for carrier collection from the various terminals to the central trunk.[49] Furthermore, the very open dendritic structure favors the efficient dispersion of gold NPs into the manganese oxide host matrix. In this regard, Figure 5b clearly reveals that Mn$_2$O$_3$ nanostructures were evenly decorated by tiny Au nanograins, which could be evidently discerned due the image contrast enabled by the large difference in manganese and gold atomic numbers (Z = 25 and 79, respectively). The average size of gold nanoaggregates was estimated to be 10 ± 3 nm (Figure 5c), consistently with SEM data. Their high dispersion, relatively low amount and small size account for the lack of detectable Au reflections in the recorded XRD patterns (see above and Figure 1). Nonetheless, Figure 5c also clearly reveals a very intimate host–guest contact, with gold NPs embedded into the manganese oxide hosts. These findings are in line with the occurrence of a SMSI,[27,28,30–32] whose influence on the material electrochemical performances will be discussed later.

Additional important information could be gained by the combined use of high angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) imaging and simultaneous EDXS chemical mapping (Figure 5d). These analyses revealed that gold nanoparticles were predominantly located in the near-surface regions of manganese oxide dendrites, following the landscape of Mn$_2$O$_3$ “trees.” Nevertheless, a careful image inspection enabled to observe a certain in-depth Au dispersion throughout the entire structure, in accordance with SIMS results (see above and Figure 3).

In the case of Mn$_2$O$_3$-based specimens, TEM analyses yielded qualitatively similar characteristics concerning both the deposit structure and the spatial distribution of Au particles (see Figure S4 in the Supporting Information). The morphological features of the obtained materials and the intimate contact between gold aggregates and the underlying manganese oxides is indeed an important issue to profitably exploit their mutual electronic and chemical interplay, ultimately yielding an appreciable performance enhancement in comparison to bare Mn$_2$O$_3$.

The OER performances of the developed FTO-supported electrocatalysts were preliminarily investigated in 0.5 m KOH aqueous solutions. Figure 6a displays the linear sweep voltammetry (LSV) curves for bare and gold-decorated Mn$_2$O$_3$ (MnO$_2$,
Figure 5. a) Plane-view SEM image of a Mn$_2$O$_3$ specimen functionalized with Au nanoparticles. The region marked by the white rectangle is displayed as an enlargement in panel A. b) Low magnification cross-sectional bright field-TEM image of the same specimen. c) High resolution-TEM (HR-TEM) image of selected Au nanoparticles deposited on Mn$_2$O$_3$. In panels (b) and (c), the dark contrast Au nanoparticles are marked by white arrows. d) Cross-sectional high angle annular dark field-scanning TEM (HAADF-STEM) image and corresponding energy dispersive X-ray spectroscopy (EDXS) mapping of Mn K (green), Au M (red), and O K (blue) lines. An overlayed map superimposing manganese, gold and oxygen X-ray signals is presented in the bottom right corner panel.
Mn₂O₃) samples. As a general rule, current density (j) values increased with the applied potential (Eₗ), indicating a progressively more effective water oxidation at the electrode surface. Interestingly, catalytic activity systematically increased in the order MnO₂ < Au/MnO₂ << Mn₂O₃ < Au/Mn₂O₃, indicating that: (i) Mn₂O₃ was much more active than MnO₂; (ii) for both MnₓOₙ polymorphs, the introduction of gold NPs enhanced OER performances. Concerning issue (i), it is worth recalling that MnO₂ and Mn₂O₃ matrices were prepared starting from the same Mn–O deposit (see Scheme 1) and, after thermal treatment, presented similar morphological features. Hence, since the two samples only differed in their crystal structure and related surface chemistry [i.e., Mn(IV) versus Mn(III)], the present findings highlight the superior catalytic activity of β-Mn₂O₃ (bixbyite) compared to β-MnO₂ (pyrolusite) under the adopted experimental conditions, a topic that has been a matter of debate.[9,18,25]

The current density enhancement occurring upon Mn₂O₃ decoration with gold NPs can be mainly traced back to local interfacial effects between Au and MnₓOₙ. In this regard, consistently with the above XPS data, some authors have reported that gold NPs, even in trace amounts, can donate electron density to neighboring Mn sites at the interface with Au NPs.[2,21,39] The latter phenomenon is also likely accompanied by the formation of oxygen vacancies close to the Au/MnₓOₙ interface, in line with XPS results and optical absorption spectra.[7,26,31,45] Hence, the improved OER performances of gold-containing samples with respect to bare MnₓOₙ specimens can be related to the higher content of oxygen vacancies, whose presence favorably impacts on adsorption, activation and dissociation steps.[33,35,36,38,42,44,48] Based on the above hypothesis, in good agreement with the occurrence of a SMSI effect,[27,29–32,39,43] the main role of gold NPs is to locally activate the host MnₓOₙ matrices, rendering them more effective OER catalysts.[18] Nevertheless, it is worth recalling that the higher oxygen vacancies content in Au/MnO₂ and Au/Mn₂O₃ might partially be due to a preferential oxygen removal during the sputtering step (see Scheme 1).[30,36]

Overall, j values up to ≈5 mA cm⁻² at 1.65 V versus the reversible hydrogen electrode (RHE) were obtained (see table in Figure 6). Such results are comparable, or even better than, various MnₓOₙ-based materials reported in the literature (see Table S1 in the Supporting Information),[1,2,5,9,18,19,23] candating the present systems as appealing OER electrocatalysts. In line with the above described current density trend for the various specimens, overpotentials (η) at 1 mA cm⁻² decreased following the opposite order, i.e., MnO₂ > Au/MnO₂ > Mn₂O₃ > Au/Mn₂O₃ (see Figure 6). However, the analysis of Tafel plots in Figure 6b revealed a more complex dependence on the system composition. In fact, gold-decorated samples exhibited Tafel slope values lower than the corresponding bare MnₓOₙ specimens, indicating a beneficial role of Au NPs on OER kinetics.[1,2,21,29] Yet, if MnO₂-based samples are compared with Mn₂O₃-based ones, the latter are characterized by higher values. This result, apparently in contrast with the corresponding current density and overpotential value trends, can be explained taking into account: (i) a different rate determining step and/or reaction mechanism[53] for the two manganese oxide polymorphs (the Tafel slope decreases once the rate-determining step is closer to the end step of a series of
3. Conclusions

In the present work, we have proposed an original, versatile and potentially scalable route for the fabrication of Mn oxide-based electrocatalysts and for the enhancement of their OER performances. Characterization results revealed indeed the possibility to achieve the selective formation of the desired MnO$_x$ (MnO$_2$, Mn$_3$O$_4$) polymorph featuring an open dendritic morphology and a high content of oxygen vacancies. In addition, the eventual decoration of the obtained Mn$_2$O$_3$ nanomaterials with MnO$_2$ nanoparticles was able to further increase the catalytic activity for the OER.

Subsequently, functionalization with gold nanoparticles was performed by RF-sputtering from Ar plasmas using the same instrumentation. The obtained manganese oxides were used as substrates and mounted on the grounded electrode, whereas a gold target (BALTEC AG, 99.99%) was fixed on the RF one. RF-sputtering was carried out under optimized conditions, that enabled to avoid a complete manganese oxide coverage by a continuous gold overlayer (growth temperature = 60 °C, total pressure = 0.3 mbar, Ar flow rate = 10 ± 1 sccm, RF-power = 5 W, sputtering time = 30 min).

Finally, ex situ thermal treatment was performed at 500 °C for 60 min, under Ar or air to induce the formation of Mn$_3$O$_4$ or MnO$_2$-based electrodes [38] respectively.

Characterization: XRD patterns were collected with a Bruker D8 Advance diffraction meter equipped with a Göbel mirror, using a CuKα X-ray source operated at 40 kV and 40 mA. The patterns were acquired in the 16-52° 2θ range (0.03° × step$^{-1}$ and 10 s × step$^{-1}$).

XPS analyses were performed by a Perkin-Elmer Phi 5600-ci spectrometer using a standard Al Kα radiation (1486.6 eV). The sample analysis area was 800 µm in diameter. Due to the Mn$_3$O$_4$ and Au4f photoelectron peak overlap, quantitative analysis was based on the interference-free Au4d$_{5/2}$ signal. [37] BE values (by default = ±0.2 eV) were corrected for charging by assigning to the adventitious C1s peak a BE value of 284.8 eV. Data analysis involved Shirley-type background subtraction and peak area determination by integration, eventually using nonlinear least-squares curve fitting adopting Gaussian–Lorentzian fitting.

Atomic compositions were evaluated from peak areas using sensitivity factors supplied by Perkin Elmer. Calculation of the Au/Mn atomic surface ratio was carried out basing on a previously reported report. [35] For gold, the use of the most intense Au4f peak was intentionally avoided due to its overlap to the Mn3s and MnO$_2$-based peaks.

Optical absorption spectra were registered by means of a Cary 50 (Varian) dual-beam spectrophotometer (spectral bandwidth = 1 nm), operating in transmission mode and at normal incidence. In each spectrum, the FTO substrate contribution was subtracted. Extrapolation of band gap values was performed using the Tauc equation ($\alpha h\nu$)$^2$ versus $h\nu$, where $\alpha$ is the absorption coefficient, assuming direct and allowed transitions for both Mn$_2$O$_3$ and Mn$_3$O$_4$-based systems. [32,22,23]

Plane-view and cross-sectional FE-SEM images were recorded by means of a Zeiss SUPRA 40VP microscope, operating at primary beam acceleration voltages of 10 kV and collecting electrons by means of an in-lens detector. The mean deposit thickness and particle dimensions were estimated using the ImageJ software. [38]

AFM images were recorded using an NT-MDT SPM Solver P47H-PRO apparatus, operating in semicontact mode. All measurements were performed in air at room temperature. RMS roughness values were obtained from the height profiles of 3 × 3 µm$^2$ images, after background subtraction.

Thin cross-sectional samples for TEM characterization were prepared by the focused ion beam technique (FIB), using a Helios 600i FIB/SEM instrument (Thermo Fisher, USA). Prethinned lamellas were lifted out from the target material, attached to a TEM grid and subsequently thinned to electron transparency. Final cleaning was performed by FIB, operating at 5 kV and low current (25 pA). During sample preparation, when necessary, a Pt protective layer was deposited over the structures to embed them and prevent them from collapsing. HR-TEM, HAADF-STEM, and EDXS analyses of Mn$_2$O$_3$-based specimens were performed using an aberration double-corrected cold FEG JEM ARM200F apparatus operated at 200 kV, equipped with a CENTURIO EDXS detector, ORIUS.
Catan camera and Quantum GIF. Analyses on MnO₂-based specimens were carried out by an aberration corrected FEI Titan™ 60-300 kV microscope operated at 300 kV.

**Electrochemical Tests:** The electrochemical performances of the target systems towards OER were assessed by three-electrode setup, using a VM3P (BioLogic Science Instruments) working station. A Pt mesh, a Hg/HgO (MMO) electrode and the target FTO-supported materials were used as the counter, reference and working electrodes, respectively. The potential was transformed into the RHE scale using the relation [9]

\[ E_{\text{RHE}}(V) = E_{\text{MMO}}(V) + 0.0592 \times \text{pH} + 0.111 \]  

The presented electrochemical data do not include compensation for the series resistance of the solution. LSV curves were registered in freshly prepared 0.5 m KOH solutions at a scan rate of 1 mV s⁻¹, and the measured currents were normalized to the electrode geometric area (1.0 ± 0.2 cm²; uncertainty on current density values = 0.05 mA cm⁻²). The OER overpotential (η, uncertainty = ±2 mV) at 1 mA cm⁻² was calculated as [10,15–20,23]

\[ \eta(V) = \frac{E_{\text{WE}}(V \text{ vs RHE}) - 1.23}{\text{t} \text{afel}} \]  

where \( E_{\text{WE}} \) and 1.23 are the measured potential value and the standard potential of O₂ evolution versus RHE, respectively. Tafel slopes (uncertainty = ±1 mV per decade) were obtained by plotting \( E_{\text{WE}} \) versus the current density logarithm.[14,18–20,19]

### Supporting Information

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

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

manganese oxides, oxygen evolution reaction, strong metal–support interaction

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