Doped-MoSe$_2$ Nanoflakes/3d Metal Oxide–Hydr(Oxy) Oxides Hybrid Catalysts for pH-Universal Electrochemical Hydrogen Evolution Reaction

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1. Introduction

2D-transition metal dichalcogenides (TMDs), whose crystal structure is composed by covalently bonded X-M-X (M = transition metal; X = chalcogen) layers held together by van der Waals forces,[1–3] have been reported as noble, metal-free, highly efficient, and stable electrocatalysts for electrochemical hydrogen evolution reaction (HER).[4–9] Theoretical[10–13] and experimental[14–17] investigations have demonstrated that the unsaturated X-edges in the natural semiconducting trigonal prismatic 2H phase of TMDs are HER electrocatalytically active in acidic media, with a Gibbs free energy of adsorbed atomic H ($\Delta G_{\text{Hads}}$) close to zero.[10,12] Consequently, extensive efforts have been dedicated to increasing the number of exposed active sites, including the design of nanostructured films (e.g., double-gyroid mesoporous[16] and vertically aligned nanostructures[18,19]), the engineering of the stoichiometry of the catalytically inert basal plane by defective[20,21] and doping treatments,[8,9,22–24] as well as the developments of hybrid materials (e.g., CoS$_x$/MoS$_2$,[23] MoS$_2$/Mo$_2$C,[26] and graphene/or carbon nanotubes (CNTs)/TMDs[27–29] and Ni/TMDs[30,31]). Despite the recent progress, there are still experimental issues that need to be resolved before TMDs can be considered an economical material platform for the production of H$_2$, including: 1) the scalability of the synthesis of high active electrocatalysts; 2) the potential cost/benefit of the hybridization strategies; 3) the feasibility of the electrode cell assembly; and 4) the HER-activity and stability in both acidic and alkaline electrolytes. In fact, it is still challenging to design scalable and cost-effective pH-universal TMD-based electrocatalysts[23,32] that are capable of competing with cathode materials found in current large-scale H$_2$ production technologies[33,34] such as Ni alloys[35,36] or high surface area noble metal-coated Ni[37] for chloro-alkaline or alkaline...
zero gap water\(^{38}\) electrolysis units, and Pt nanoparticles supported on carbon black (Pt/C) for proton exchange membrane electrolysis.\(^{39–41}\)

Herein, we report the design of pH-universal efficient HER-electrocatalysts based on doped-MoS\(_2\) flakes/3d metal oxide–hydr(oxy)oxide hybrids by the cost-effective material production and electrode manufacturing through solution-processed methods in an environmentally friendly alcohol-based solvent. Our electrodes achieved low overpotential at a cathodic current density of 10 mA cm\(^{-2}\) \((\eta_{	ext{ho}})\) of 0.081 and 0.064 V in 0.5 M H\(_2\)SO\(_4\) and 1 M KOH, respectively, as well as promising electrochemical stability under HER-operation, fulfilling the key-requirements for practical applications.

2. Results and Discussion

2.1. Production and Characterization of Materials

Amongst the TMDs, we focused our attention on MoSe\(_2\) because it has a higher intrinsic electrical conductivity and a lower \(\Delta E_g\)^0 at the edge sites than other TMDs.\(^{28,42,43}\) MoSe\(_2\) nanoflakes were produced by a cost-effective liquid-phase exfoliation (LPE)\(^{44–47}\) of the bulk counterpart in 2-Propanol (IPA), followed by a sedimentation-based separation\(^{48–50}\) (see the Experimental Section for the additional details of the synthesis of materials). Figure 1a,b shows transmission electron microscopy (TEM) and atomic force microscopy (AFM) images of the as-exfoliated MoSe\(_2\) (ex-MoSe\(_2\)), whose morphology resembles a crumpled paper-like structure. Statistical analysis indicates that the ex-MoSe\(_2\) have a lateral size in the range of 10–170 nm and 3 nm) (Figure 1c) and a thickness up to almost 10 nm (log normal distribution peaked at \(\approx\)3 nm) (Figure 1d). Thus, single/few layer ex-MoSe\(_2\) were effectively produced (MoSe\(_2\) monolayer thickness has been previously measured between 0.6 and 1 nm\(^{51,52}\)).

The ex-MoSe\(_2\) flakes were subsequently doped through 3d transition metal (Fe, Co, Ni, Cu, Zn, Cd) chloride (MCl\(_2\)) chemical doping.\(^{53–55}\) Experimentally, the MCl\(_2\)-chemical doping of the ex-MoSe\(_2\) was carried out by mixing an ex-MoSe\(_2\) dispersion with a MCl\(_2\) solution in anhydrous IPA, in which the MCl\(_2\) dissociate in M\(^{2+}\) and 2Cl\(^{-}\) (being the MCl\(_2\) solution concentration (0.4 g L\(^{-1}\)) inferior to the solubility limit of MCl\(_2\) in alcohol, \(\geq 1\) g L\(^{-1}\).\(^{56,57}\) thus obtaining ex-MoSe\(_2\):MCl\(_2\) dispersions in IPA (1:1 molar ratio). These underwent an ultrasonication treatment, during which we suppose a doping process occurred via “cascade reaction” as follows:

Step 1:

\[
\begin{align*}
\text{a) } & \text{ex-MoSe}_2 + M^{2+} + 2\text{Cl}^{-} \rightleftharpoons \text{ex-MoSe}_{2}^{2+} + M^{0} + 2\text{Cl}^{-} \text{ and/or} \\
\text{b) } & \text{ex-MoSe}_2 + 2M^{2+} + 4\text{Cl}^{-} \rightleftharpoons \text{ex-MoSe}_{2}^{2+} + M^{0} + \text{MCl}_4^{2-}
\end{align*}
\]

Step 2:

\[
\begin{align*}
\text{a) } & \text{ex-MoSe}_{2}^{2+} + 2\text{Cl}^{-} \rightleftharpoons \text{ex-MoSe}_2 - 2\text{Cl} \text{ and/or} \\
\text{b) } & \text{ex-MoSe}_{2}^{2+} + \text{MCl}_4^{2-} \rightleftharpoons \text{ex-MoSe}_2 - \text{MCl}_4
\end{align*}
\]

The doping mechanism is initiated by an electron transfer from ex-MoSe\(_2\) to M\(^{2+}\) (step 1). This is caused by the high electronegativity of the latter, which has been theoretically estimated in an aqueous solution-phase as 2.636, 2.706, 2.891, 2.952, 2.796, and 2.660 Pauling units for Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), and Cd\(^{2+}\), respectively.\(^{58}\) These values agree with the Irving–Williams order of transition metal complexes\(^{59}\) and they have to be considered as underestimations in comparison with those that correspond to an IPA-solution because of the higher polarity of the H\(_2\)O (\(\approx\)10.2),\(^{56}\) whose solvation weakens the electron-accepting power of cations\(^{58,61}\) than that of IPA (\(\approx\)3.9).\(^{57}\) A similar doping initiation has been proposed for MCl\(_2\)- and MCl\(_2\) doped graphene\(^{62,63}\) and CNTs.\(^{64}\) Lastly, a neutralization of the charged species (MoSe\(_2\)^{2–}) and MCl\(_2\), MCl\(_4\)^2–, and Cl\(^{-}\) occurs by creating ex-MoSe\(_2\)–2Cl and ex-MoSe\(_2\)–MCl\(_4\) complexes (step 2). Here, the electron cloud shifts toward the Cl-based centers, creating a net charge displacement, leading to a p-type doping of the ex-MoSe\(_2\).\(^{62–64}\) Notably, the electron depletion of MCl\(_2\)-doped TMD nanoflakes has been previously exploited for designing p-doped Mo\(_2\)S\(_2\)-based hole transport layers in organic solar cells\(^{65}\) and H\(_2\)-evolving photocathodes.\(^{66}\)

The chemical and electronic state within the exposed surfaces of MCl\(_2\)-doped ex-MoSe\(_2\) (ex-MoSe\(_2\):MCl\(_2\)) were evaluated by X-ray photoelectron spectroscopy (XPS) analysis (Figure 1e–g). Figure 1e,f shows the Mo 3d and Se 3d XPS spectra of ex-MoSe\(_2\):MCl\(_2\) (except for M = Cu). These data evidence a uniform shift (in the range of 0.1–0.4 eV) toward a lower binding energy compared to those of the as-produced ex-MoSe\(_2\). This indicates that the amount of energy that is required to remove an electron from the ex-MoSe\(_2\):MCl\(_2\) surface is lower than that needed for the ex-MoSe\(_2\) that means that the electronic density in the ex-MoSe\(_2\) surface increases after MCl\(_2\)-doping. Actually, the downshift also agrees with the decrease of the Fermi level upon the p-type MCl\(_2\)-doping of ex-MoSe\(_2\) and the upward band-bending appearance localized at the doped/undoped regions’ interface.\(^{53,67,68}\) In the Mo 3d spectra (Figure 1e), the two peaks located at \(\approx\)229 and \(\approx\)232 eV are attributed to the Mo 3d\(_{3/2}\) and Mo 3d\(_{1/2}\) peaks of the Mo\(^{4+}\) state in MoSe\(_2\).\(^{69,70}\) The distinct binding energy peaks associated with the M 2p or 3d doublets (Figure 1g) are ascribed to the oxidized states of M (i.e., Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), or Cu\(^{2+}\)) or metal hydr(oxy)oxides (e.g., M(OH)\(_2\) for M\(^{2+}\) or M(OH)\(_1\) and M(OH)\(_0\) for M\(^{4+}\)) originating from the reaction between M\(^{2+}\) and O\(_2\) or H\(_2\)O, after exposure to ambient. Additional details of the XPS analysis are reported in the Supporting Information. In short, XPS data show that metal oxide/hydr(oxy)oxides have been formed in situ on the surface of the ex-MoSe\(_2\), creating doped-MoSe\(_2\) nanoflakes/3d metal oxide-hydr(oxy)oxides hybrids. The structural topological properties of the ex-MoSe\(_2\) and ex-MoSe\(_2\):MCl\(_2\), as well as those of their MoSe\(_2\) bulk counterparts, were evaluated by Raman spectroscopy measurements. According to group theory analysis, MoSe\(_2\) bulk is characterized by four Raman active modes: three in-plane E\(_2g\), E\(_1g\), and E\(_1g\) and one out-of-plane A\(_{1g}\) of D\(_{4h}\) point group symmetry.\(^{71–73}\) After exfoliation, the interlayer vibrational mode B\(_{2g}\) is activated by the breakdown of the translational symmetry that occurs in few-layer MoSe\(_2\) flakes.\(^{74}\) Representative spectra of MoSe\(_2\)bulk, ex-MoSe\(_2\) and...
Figure 1. Morphological, chemical, and structural characterizations of pristine and MCl₂-doped ex-MoSe₂. a) TEM image of the ex-MoSe₂. b) AFM image of ex-MoSe₂ deposited onto a mica sheet. The height profiles of two representative flakes are also shown (white line). c) TEM statistical analysis of the lateral dimension of the ex-MoSe₂ (calculated on 80 flakes). d) AFM statistical analysis of the thickness of the ex-MoSe₂ (calculated on 80 flakes from different AFM images). e,f) Mo 3d and Se 3d XPS spectra of ex-MoSe₂ and ex-MoSe₂:MCl₂. Their deconvolutions are also shown, evidencing the band ascribed to: Mo⁴⁺ and Se²⁺ (MoSe₂) (blue curves); Se 3s band (red curve), overlapping the Mo 3d XPS spectrum; Mo⁶⁺ (MoO₃) (magenta curves); Se⁰ (edge Se) (gray curves); Fe 3p band (olive curve), overlapping the Se 3s XPS spectrum. g) Fe 2p (blue curve), Co 2p (cyan curve), Cu 2p (magenta curve), Ni 2p (dark yellow curve), Zn 2p (navy curve), and Cd 3d (olive curve). h) Raman spectra of MoSe₂ bulk (black curve), ex-MoSe₂ (red curve), ex-MoSe₂:FeCl₂ (blue curve), ex-MoSe₂:ZnCl₂ (cyan curve), ex-MoSe₂:CuCl₂ (magenta curve), ex-MoSe₂:NiCl₂ (dark yellow curve), ex-MoSe₂:ZnCl₂ (navy curve), and ex-MoSe₂:CdCl₂ (olive curve), as-deposited on Si/SiO₂ substrates. The main peaks, i.e., the in-plane modes E₁₉, E₂₉, and E₃₂, the out-of-plane mode A₁₁, and the breathing mode B₂₉ are named in the graph.
ex-MoSe₂:MCl₂ are reported in Figure 1h. The A_{1g} mode is located at \(\approx 241\) cm\(^{-1}\) for the MoSe\(_2\) bulk, while it red-shifts to \(\approx 239\) cm\(^{-1}\) for the ex-MoSe\(_2\), which is in agreement with the softening of the vibrational mode that is accompanied by a reduction in flake thickness.\(^{[18,75-78]}\) The in-plane E\(_{2g}\) mode is observed at \(\approx 287\) cm\(^{-1}\) for both samples.\(^{[18,73-76]}\) The intensity ratio between the A\(_{1g}\) and E\(_{2g}\) modes (\(I(A_{1g})/I(E_{2g})\)) (\(\approx 21\)) and the presence of the B\(_{2g}\) mode (located at \(\approx 352\) cm\(^{-1}\)) in the ex-MoSe\(_2\) spectra indicate the few-layer flake structure.\(^{[75,79,80]}\) The Raman analysis is reported in Figure S1 of the Supporting Information. Although XPS analysis evidences surface modifications of ex-MoSe\(_2\) after MCl\(_2\)-doping, the presence of the Raman peaks at 241 cm\(^{-1}\) for the MoSe\(_2\) bulk indicates that the structure of undoped flakes is preserved. Therefore, doping-induced chemical modifications are excluded, suggesting that molecular van der Waals complexes have formed between ex-MoSe\(_2\)\(^{2-}\) and Cl\(^-\) or MCl\(_2\)\(^{-2}\). These complexes originated from the charge neutralization through physisorption and/or chemisorption of the ionic species to the ex-MoSe\(_2\) during the MCl\(_2\)-doping process (step 2).\(^{[54,81,84]}\)

### 2.2. Production and Electrochemical Characterization of Electrocatalysts

The HER-activities of ex-MoSe\(_2\) and ex-MoSe\(_2\):MCl\(_2\), which were deposited on glassy carbon substrates (ex-MoSe\(_2\) mass loading: 0.2 mg cm\(^{-2}\)), were evaluated both in acidic (0.5 m H\(_2\)SO\(_4\)) and alkaline (1 m KOH) solutions (Figure 2).

Theoretically, the HER in acid solution proceeds with an initial discharge of the hydronium ion (H\(_3\)O\(^+\)) and the formation of intermediates, i.e., atomic H adsorbed on the electrocatalyst surface (H\(_{ads}\)), in the so-called Volmer step (H\(_3\)O\(^+\) + e\(^-\) \(\rightarrow\) H\(_{ads}\) + H\(_2\)O), followed by either an electrochemical Heyrovsky step (H\(_{ads}\) + H\(_3\)O\(^+\) + e\(^-\) \(\rightarrow\) H\(_2\) + H\(_2\)O) or a chemical Tafel recombination step (2H\(_{ads}\) \(\rightarrow\) H\(_2\)). In alkaline media, the H\(_{ads}\) is formed by discharging H\(_2\)O (H\(_2\)O + e\(^-\) \(\rightarrow\) H\(_{ads}\) + OH\(^-\)). Then, either a Heyrovsky step (H\(_2\)O + H\(_{ads}\) + e\(^-\) \(\rightarrow\) H\(_2\) + OH\(^-\)) or a chemical Tafel recombination step (2H\(_{ads}\) \(\rightarrow\) H\(_2\)) occurs. The overpotential at a cathodic current density of 10 mA cm\(^{-2}\) (\(\eta_{10}\)) is the figure of merit (FoM) that are needed to assess the HER-activity.\(^{[85,86]}\) The last two of these FoM can be extracted from the linear portion of the Tafel plots, which show the relation between the overpotential and the current density of the electrodes, and are in agreement with the Tafel equation (see the Experimental Section for characterization of electrodes). The Tafel slope measures the potential increase that is required to improve the current density by one order of magnitude. Fundamentally, it is used to evaluate the HER mechanism at the electrode/electrolyte interface.\(^{[85,86]}\) For an insufficient H\(_{ads}\) surface coverage, the Volmer reaction is the rate limiting step of the HER, and a theoretical Tafel slope of 120 mV dec\(^{-1}\) is observed. On the other hand, for a borderline case in which there is a high H\(_{ads}\) surface coverage (i.e., in which the \(\Delta G_{H_{ads}}\) is close to zero), the HER-kinetic is dominated by the Heyrovsky or Tafel reaction, and a Tafel slope of 40 or 30 mV dec\(^{-1}\) is detected. The \(\eta_{10}\) is linked to the number of available HER-active sites and their HER-kinetics.\(^{[85,86]}\) Figure 2a,b shows linear sweep voltammetry (LSV) curves of ex-MoSe\(_2\) and ex-MoSe\(_2\):MCl\(_2\), in acidic and alkaline solutions, respectively, while Figure 2c,d reports the corresponding Tafel plots. The extrapolated \(\eta_{10}\) are reported in Figure 2e. The LSV data show that the HER-activity of ex-MoSe\(_2\) was affected by the MCl\(_2\)-doping.

In the acidic solution, the ex-MoSe\(_2\) doped with CdCl\(_2\), ZnCl\(_2\), CuCl\(_2\), and NiCl\(_2\) showed higher cathodic current densities than the pristine ex-MoSe\(_2\), while the CoCl\(_2\) and FeCl\(_2\)-doping decreased the HER-activity. Thus, the \(\eta_{10}\) decreased from 0.445 V for the ex-MoSe\(_2\):FeCl\(_2\) to 0.235 V for the most active case of ex-MoSe\(_2\):CdCl\(_2\). The Tafel slope of ex-MoSe\(_2\):NiCl\(_2\) significantly decreased from 0.102 V dec\(^{-1}\) in the ex-MoSe\(_2\) to 0.065 V dec\(^{-1}\), while it was marginally affected by CoCl\(_2\), CuCl\(_2\), ZnCl\(_2\), and CdCl\(_2\)-doping (Figure 2c,d). The \(j_0\) was significant affected by NiCl\(_2\)-doping, but there was no remarkable variation for the others MCl\(_2\)-dopings (Figure S2, Supporting Information). In the alkaline solution, CoCl\(_2\) and NiCl\(_2\) were the most effective dopants for increasing the HER-activity of the ex-MoSe\(_2\). The corresponding \(\eta_{10}\) were 0.308 V and 0.273 V, respectively, which were lower than that of the ex-MoSe\(_2\) (0.349 V). CdCl\(_2\) and ZnCl\(_2\) dopants did not significantly affect the ex-MoSe\(_2\) HER-activity, which decreased for both ex-MoSe\(_2\):CuCl\(_2\) and ex-MoSe\(_2\):FeCl\(_2\).

As was the case in the acidic media, NiCl\(_2\) was the most effective dopant for decreasing the Tafel slope of the ex-MoSe\(_2\) (from 0.147 to 0.114 V dec\(^{-1}\)). The ex-MoSe\(_2\) and the ex-MoSe\(_2\):MCl\(_2\) displayed comparable \(j_0\) values (in the range of 10–30 \(\mu\)A cm\(^{-2}\)), with the only exception of ex-MoSe\(_2\):CuCl\(_2\), which showed a higher \(j_0\) value (around 70 \(\mu\)A cm\(^{-2}\)). These results indicate that MCl\(_2\)-doping can be effective in enhancing the HER-activity of ex-MoSe\(_2\) in both acidic and alkaline solutions.

Once the HER-activity of the ex-MoSe\(_2\):MCl\(_2\) had been established, flexible, self-standing heterostructures between single-walled carbon nanotubes (SWCNTs) and ex-MoSe\(_2\):MCl\(_2\) (SWCNTs/ex-MoSe\(_2\):MCl\(_2\)), produced via the sequential vacuum filtration of the SWCNTs and ex-MoSe\(_2\):MCl\(_2\), were investigated as flexible HER-active electrodes compatible with high-throughput scalable industrial manufacturing. The rationale of the choice of these heterostructures was based on our recent works\(^{[87,88]}\) in which we demonstrated a long-range (21 \(\mu\)m) electrochemical coupling between TMDs and graphene or SWCNT bucky paper (substrates)\(^{[89,90]}\) for increasing the HER-activity of TMDs, without resoring the synthesis of hybrid TMDs/carbon material compounds.\(^{[28-31]}\)

Figure 3a,b reports the top-view scanning electron microscopy (SEM) images of the SWCNT paper (SWCNT mass loading: 0.64 mg cm\(^{-2}\)) and SWCNTs/ex-MoSe\(_2\) (SWCNTs mass loading: 0.64 mg cm\(^{-2}\); ex-MoSe\(_2\) mass loading: 0.64 mg cm\(^{-2}\)).

The surface of the SWCNT paper consists of a mesoporous network with a bundle-like arrangement (Figure 3a). The surface of the SWCNT paper is clearly modified by the ex-MoSe\(_2\) overlay (Figure 3b), which is characterized by the flaked nature of the ex-MoSe\(_2\) (see TEM and AFM analysis, Figure 1). The AFM images of the electrode surfaces (Figure S3, Supporting Information; Figure 3c) evidence morphologies similar to those observed by SEM. The calculated roughness average (Ra)
values are $\approx 103$ and $\approx 70$ nm for SWCNT paper and SWCNTs/ex-MoSe$_2$ surfaces, respectively. These values indicate that the ex-MoSe$_2$ deposition flattens the SWCNT paper surface. The top-view SEM image of a representative SWCNTs/ex-MoSe$_2$:NiCl$_2$ (Figure 3d) does not evidence any significant surface changes in comparison to that of SWCNT/ex-MoSe$_2$. The cross-sectional SEM images of SWCNTs/ex-MoSe$_2$:NiCl$_2$ (Figure 3e) shows a bilayer-like architecture. The thickness of the ex-MoSe$_2$:NiCl$_2$ overlay is $\approx 1$ $\mu$m. The elemental energy-dispersive X-ray spectroscopy (EDX) analysis of a top view SEM image of SWCNTs/ex-MoSe$_2$:NiCl$_2$ (Figure S4, Supporting Information) shows the uniform distribution of Ni onto the heterostructure’s surface, thus indicating that the NiCl$_2$-doping of ex-MoSe$_2$ is uniform. Interestingly, the EDX analysis of a cross-sectional SEM image of SWCNTs/ex-MoSe$_2$:NiCl$_2$ (Figure S5, Supporting Information) reveals that Ni is also distributed uniformly along the vertical direction of the heterostructure, including the SWCNT paper. This means that, during deposition of the ex-MoSe$_2$:MCl$_2$, the elemental metal (i.e., M$^{0}$) and, eventually, the MCl$_2$ residuals also infiltrated the SWCNT paper. Thus, the formation of metal oxides (MO or M$_2$O$_3$) or metal hydr(oxy)oxides (M(OH)$_2$, M(OH)$_3$, or MO(OH)) on SWCNT paper and the p-doping of the SWCNTs [64] can also occur during the fabrication of the heterostructures. It is worth noting that the p-doping of the SWCNTs can enhance the electron transfer from the SWCNT papers to the active sites of ex-MoSe$_2$:MCl$_2$, as experimentally observed on a highly sensitive, p–n heterojunction diode-photodetector with a fast response ($<$ 15 $\mu$s) and tuneable gate using SWCNTs and single-layer MoS$_2$ as p-type and n-type semiconductors.[91] Figure 3f,g shows top-view and side-view photographs of SWCNTs/ex-MoSe$_2$:NiCl$_2$. The picture in Figure 3g was taken on manually bended SWCNTs/ex-MoSe$_2$:NiCl$_2$ in order to illustrate its mechanical flexibility, which can enable versatile designs to be exploit for advanced solar fuel devices including flexible photoelectrochemical cells[92,93] and H$_2$ storage systems [93–95]. Actually, the designed heterostructures also offer interconnected pores which improve the transport of evolved H$_2$,[96,97] enabling multiple
heterostructure to be stacked in a single electrode. Therefore, 2- and 4-stacked heterostructures were then assembled (Figure 3h). The monolithical stacking potentially allow the electrodes to fulfill the areal performance requirements of energy renewable buffer units (cathodic current density > 100 mA cm$^{-2}$ at an overpotential less than 200 mV).[33–41] It must be highlighted that, by selecting the number of heterostructures, the mass loading of the active materials is no longer limited as is the case with the single heterostructures, in which the fragmentation of films with a mass loading superior to a few mg cm$^{-2}$ occur during their deposition and/or HER-operation (i.e., gas evolution).[98]

Figure 4a,b report the iR-corrected LSV curves of the SWCNTs/ex-MoSe$_2$:CdCl$_2$ and SWCNTs/ex-MoSe$_2$:NiCl$_2$ in acidic and alkaline solutions, respectively, together with those of the 2- and 4-stacked corresponding heterostructures (labeled as: 2-SWCNTs/ex-MoSe$_2$:CdCl$_2$ and 2-SWCNTs/ex-MoSe$_2$:NiCl$_2$; 4-SWCNTs/ex-MoSe$_2$:CdCl$_2$ and 4-SWCNTs/ex-MoSe$_2$:NiCl$_2$). The LSV curves of SWCNTs/ex-MoSe$_2$:NiCl$_2$ and SWCNTs/ex-MoSe$_2$:CoCl$_2$ in acidic and alkaline solutions, respectively, are also reported for comparison (ex-MoSe$_2$:NiCl$_2$ and ex-MoSe$_2$:CoCl$_2$ were the second most HER-active ex-MoSe$_2$:MCl$_2$ in the aforementioned solutions). The LSV curves of commercial Pt/C are also shown as benchmark. These results show that the most HER-active hybrid heterostructures are those based on ex-MoSe$_2$:CdCl$_2$ and ex-MoSe$_2$:NiCl$_2$, in acidic and alkaline solutions, respectively, thus proving that the MCl$_2$-doping and the electrochemical coupling between SWCNTs and ex-MoSe$_2$ had a superimposed HER-assistive effect. Notably, the 4-stacked heterostructures yielded current densities higher than 100 mA cm$^{-2}$ at an overpotential lower than 0.2 V, both in acidic and alkaline media. A rigorous kinetic analysis of the HER, i.e., the establishment of the Tafel slope and the $j_0$, was not carried out because of the unambiguous results that derive from the presence of the SWCNT paper. In fact, SWCNTs hold a high surface area, which leads to a remarkable capacitive current density (in the order of 1 mA cm$^{-2}$) even at a low LSV sweep voltage rate ($\leq$ 5 mV s$^{-1}$). This can be the cause of misleading interpretations of the estimated kinetic parameters.[99] Thus, the HER-activity was evaluated only by analysing the $\eta_{10}$, as extrapolated from LSV measurements (Figure 2c,d).

Table 1 lists the $\eta_{10}$ values that have been measured for the different electrodes (including those using glassy carbon as a substrate, Figure 2) in both acidic and alkaline media. In the acidic medium, the $\eta_{10}$ was 0.13 and 0.16 V for SWCNTs/ex-MoSe$_2$:CdCl$_2$ and SWCNTs/ex-MoSe$_2$:NiCl$_2$, respectively. After stacking the SWCNTs/ex-MoSe$_2$:CdCl$_2$ heterostructures, the $\eta_{10}$ decreased to 0.081 V for 4-SWCNTs/ex-MoSe$_2$:CdCl$_2$. In the
alkaline medium, the $\eta_{10}$ was 0.14 and 0.22 V for SWCNTs/ex-MoSe$_2$:NiCl$_2$ and SWCNTs/ex-MoSe$_2$:CoCl$_2$, respectively. After stacking the SWCNTs/ex-MoSe$_2$:NiCl$_2$, the $\eta_{10}$ decreased to 0.064 V for 4-SWCNTs/ex-MoSe$_2$:NiCl$_2$. Notably, the heterostructures’ stacking, together with MCl$_2$ doping and SWCNTs/ex-MoSe$_2$:MCl$_2$ coupling, was effective in reaching $\eta_{10}$ which approach those of noble metal-based HER-catalysts in both acidic and alkaline media.[100–102] Actually, 4-SWCNTs/ex-MoSe$_2$:CdCl$_2$ and ex-MoSe$_2$:NiCl$_2$ deposited on glassy carbon in 0.5 H$_2$SO$_4$ (e); ex-MoSe$_2$:NiCl$_2$ and ex-MoSe$_2$:CoCl$_2$ deposited on glassy carbon in 1 M KOH (f). The insets of panels show the chronoamperometry measurements of ex-MoSe$_2$:CdCl$_2$ and ex-MoSe$_2$:NiCl$_2$ deposited on glassy carbon in 0.5 H$_2$SO$_4$ (e); ex-MoSe$_2$:NiCl$_2$ and ex-MoSe$_2$:CoCl$_2$ deposited on glassy carbon in 1 M KOH (f).

Figure 4. Electrochemical characterization of the HER-activity of hybrid heterostructures (SWCNTs/ex-MoSe$_2$:MCl$_2$) and monolithically 2- or 4-stacked heterostructures (2-SWCNTs/ex-MoSe$_2$:MCl$_2$ or 4-SWCNTs/ex-MoSe$_2$:MCl$_2$). a) LSV curves for SWCNTs/ex-MoSe$_2$:CdCl$_2$, 2-SWCNTs/ex-MoSe$_2$:CdCl$_2$, 4-SWCNTs/ex-MoSe$_2$:CdCl$_2$ and SWCNTs/ex-MoSe$_2$:NiCl$_2$ in 0.5 M H$_2$SO$_4$ (pH 1). The LSV curve of commercial Pt/C is also shown for comparison. b) LSV curves for SWCNTs/ex-MoSe$_2$:NiCl$_2$, 2-SWCNTs/ex-MoSe$_2$:NiCl$_2$, 4-SWCNTs/ex-MoSe$_2$:NiCl$_2$ and SWCNTs/ex-MoSe$_2$:CoCl$_2$ in 1 M KOH (pH 14). The LSV curve of commercial Pt/C is also shown for comparison. c,d) Comparison between the $\eta_{10}$ corresponding to LSV curves in (a) and (b). e,f) Chronoamperometry measurements ($j$–$t$ curves) at a fixed potential of –0.18 V versus RHE for: SWCNTs/ex-MoSe$_2$:CdCl$_2$ and SWCNTs/ex-MoSe$_2$:NiCl$_2$ in 0.5 M H$_2$SO$_4$ (e); SWCNTs/ex-MoSe$_2$:NiCl$_2$ and SWCNTs/ex-MoSe$_2$:CoCl$_2$ in 1 M KOH (f). The insets of panels show the chronoamperometry measurements of ex-MoSe$_2$:CdCl$_2$ and ex-MoSe$_2$:NiCl$_2$ deposited on glassy carbon in 0.5 H$_2$SO$_4$ (e); ex-MoSe$_2$:NiCl$_2$ and ex-MoSe$_2$:CoCl$_2$ deposited on glassy carbon in 1 M KOH (f).
measurements at a fixed potential of -0.18 V versus reversible hydrogen electrode (RHE) for SWCNTs/ex-MoSe2:CDCl2 and SWCNTs/ex-MoSe2: NiCl2 in the acidic medium, and SWCNTs/ex-MoSe2: NiCl2 and SWCNTs/ex-MoSe2:CoCl2 in the alkaline medium. In the acidic medium (Figure 5a) the SWCNTs/ex-MoSe2: CDCl2 and the SWCNTs/ex-MoSe2: NiCl2 slightly degraded, retaining ~86% and ~84%, respectively, of the initial current densities. This electrochemical performances reduction could be attributed to both material degradation in acidic solution and mechanical stresses generated by intense H2 bubbling (corresponding to a starting current density > 200 mA cm\(^{-2}\)) during the measurements. Actually, ex-MoSe2 has been demonstrated to be stable in 1 M H\(_2\)SO\(_4\) in our previous work.[88] However, metal oxide–hydr(ox)ides dissolution in acid could also occur. In order to monitor the possible release of metals during chronoamperometry measurements, elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed on our samples. Specifically, we carried out ICP-OES measurements on digested solutions prepared from the 0.5 M H\(_2\)SO\(_4\) solution recovered after carrying out HER measurements of ex-MoSe2:CDCl2, ex-MoSe2: NiCl2, SWCNTs/ex-MoSe2:CDCl2, and SWCNTs/ex-MoSe2: NiCl2 (additional details on sample preparation are reported in the Experimental Section). For ex-MoSe2:CDCl2 and ex-MoSe2: NiCl2, the results indicated the presence of Cd (\(\approx\)1.8 ppm) and Ni (\(\approx\)1.1 ppm), respectively. Noteworthy, for SWCNTs/ex-MoSe2:CDCl2 and SWCNTs/ex-MoSe2: NiCl2, the release of Cd decreased by ~45% (concentration of ~1.0 ppm), while Ni was not detected. This indicates that SWCNTs can suppress the physical ripening/dissolution of metal oxide–hydr(ox)ides, in agreement with the higher durability of SWCNTs/ex-MoSe2:CDCl2 and SWCNTs/ex-MoSe2: NiCl2 compared to that of ex-MoSe2:CDCl2 and ex-MoSe2: NiCl2 (inset to Figure 5a). In the alkaline medium (Figure 5b), the SWCNTs/ex-MoSe2: NiCl2 and the SWCNTs/ex-MoSe2:CoCl2 showed a catalytic activation, which increased the current densities by 13% during the first 50 min. After, the SWCNTs/ex-MoSe2: NiCl2 continued to manifest activation effects, reaching an overall increase in the current density by ~20% after 1000 min, while the SWCNTs/ex-MoSe2:CoCl2 slightly degraded, retaining ~99% of the initial current densities. Notably, similar trends were observed for the ex-MoSe2:MC12 deposited on glassy carbon, as is illustrated in the insets in Figure 5. X-ray photoelectron spectroscopy measurements revealed no chemical degradation of ex-MoSe2 during chronoamperometry measurement in alkaline solution (Figure S6, Supporting Information). It is worth to mention that the hybridization of ex-MoSe2 with metal oxide–hydr(ox)ides could also enhance the HER-durability of ex-MoSe2 in alkaline condition. In fact, recent works[104,117–119] revealed an improvement of the stability in alkaline conditions of HER-electrocatalysts, including TMDs,[104] after their hybridization with metal hydroxides, which were used to boost the HER-activity.[25,120,121] Moreover, we speculate that the activation process observed in our electrocatalysts could be caused by a structural material reorganization determined by mechanical stresses generated by H2 bubbling through the structure of the electrodes. Activation effects were significantly pronounced for

### Table 1. Summary of the overpotential at 10 mA cm\(^{-2}\) (\(\eta_0\)) for the produced electrodes in both acidic and alkaline media.

| Electrode                           | \(\eta_0\) [V] | 0.5 M H\(_2\)SO\(_4\) | 1 M KOH |
|------------------------------------|----------------|-----------------------|---------|
| ex-MoSe2                           | 0.308          | 0.445                 |         |
| ex-MoSe2:FeCl\(_2\)               | 0.445          | 0.400                 |         |
| ex-MoSe2:CoCl\(_2\)               | 0.323          | 0.308                 |         |
| ex-MoSe2:NiCl\(_2\)               | 0.248          | 0.273                 |         |
| ex-MoSe2:CuCl\(_2\)               | 0.269          | 0.403                 |         |
| ex-MoSe2:ZnCl\(_2\)               | 0.250          | 0.369                 |         |
| ex-MoSe2:CDCl\(_2\)               | 0.235          | 0.363                 |         |
| SWCNTs/ex-MoSe2:CoCl\(_2\)        | n.d.           | 0.221                 |         |
| SWCNTs/ex-MoSe2:NiCl\(_2\)        | 0.162          | 0.136                 |         |
| SWCNTs/ex-MoSe2:CDCl\(_2\)        | 0.129          | n.d.                  |         |
| 2-SWCNTs/ex-MoSe2:NiCl\(_2\)      | n.d.           | 0.116                 |         |
| 2-SWCNTs/ex-MoSe2:CDCl\(_2\)      | 0.108          | n.d.                  |         |
| 4-SWCNTs/ex-MoSe2:NiCl\(_2\)      | n.d.           | 0.064                 |         |
| 4-SWCNTs/ex-MoSe2:CDCl\(_2\)      | 0.081          | n.d.                  |         |

Figure 5. Chronoamperometry measurements (j–t curves) at a fixed potential of ~0.18 V versus RHE for: a) SWCNTs/ex-MoSe2:CDCl2 and SWCNTs/ex-MoSe2:NiCl2 in 0.5 M H\(_2\)SO\(_4\); b) SWCNTs/ex-MoSe2:NiCl2 and SWCNTs/ex-MoSe2:CoCl2 in 1 M KOH (f). The insets of panels show the chronoamperometry measurements of ex-MoSe2:CDCl2 and ex-MoSe2:NiCl2 deposited on glassy carbon in 0.5 M H\(_2\)SO\(_4\) (e); ex-MoSe2:NiCl2 and ex-MoSe2:CoCl2 deposited on glassy carbon in 1 M KOH (f).
2.3. Hydrogen Evolution Reaction-Activity Explanation

In order to explain the HER-assistive role of both the MCl₂-doping and the heterostructure design, we hypothesize multiple synergistic functional effects (Figure 6).

Concerning the MCl₂-doping, these effects include: 1) the modulation of the electronic state of ex-MoSe₂, which will improve its intrinsic electrical conductivity (passing from ≈10 GΩ cm for ex-MoSe₂ film to 700 kΩ cm for the representative doped film of ex:MoSe₂:NiCl₂, as estimated by van der Pauw resistivity measurements), i.e., the fastening charge transfer toward the HER-active sites (Figure 6a); 2) an increase in the electronic density of the ex-MoSe₂ and the local upward band-bending emergence at the p-doped/undoped regions of ex-MoSe₂:MCl₂ (see XPS analysis, Figure 1e,f), tailoring the capability of the ex-MoSe₂ to adsorb H atoms, which will facilitate the H₂ diffusion through the electrodes.
thermodynamically activate the HER (Figure 6b,c)\(^{[9,22,24]}\). In alkaline solution, the promotion of \(H_2O\) discharge due to the electrocatalytic activity of metal oxide and hydr(oxy)oxide clusters, formed from M\(^{n+}\) after material exposure to oxygen/moisture (see XPS analysis, Figure 1g) or under HER-operative electrochemical conditions (which is in agreement with the corresponding Pourbaix diagrams)\(^{[122,123]}\) (Figure 6d).\(^{[103,124]}\)

Contrary to these beneficial effects, some dopants can also negatively affect the HER-activity of ex-MoSe\(_2\). First, in acidic media, the formation of metal oxides and metal hydr(oxy)oxides may passivate the HER active sites for the discharge of \(H_2O^+\) and the formation of \(H_2\)\(_{ads}\), thus causing a Volmer reaction-limited HER. Second, in metal hydr(oxy)oxides, clusters promote \(H_2O\) discharge in alkaline media by adsorbing OH on themselves along the \(H_2\)\(_{ads}\) formation on the HER-electrocatalysts.\(^{[103,124]}\) However, the rate of the desorption of \(OH_{ads}\) to regenerate the \(H_2O\) dissociative properties is critical in order to determine the resulting HER-activity.\(^{[103]}\) In more detail, the decrease in the interaction strength between the \(OH_{ads}\) and the M site of the metal hydr(oxy)oxide has been correlated to the HER activity increase in metal hydr(oxy)oxide/Pt (following the order \(Ni > Co > Fe\)).\(^{[103]}\) Therefore, the HER-activity of ex-MoSe\(_2\):MCl\(_2\) in alkaline media is expected to have a similar dependence on M to that of metal hydr(oxy)oxide/Pt. These expectations are in agreement with our experimental measurements, where NiCl\(_2\) and FeCl\(_2\) dopants have led to a maximum and minimum, respectively, ex-MoSe\(_2\) HER-activity at pH 14 (Figure 2).

By optimizing the amount of MCl\(_2\) doping and investigating different ex-MoSe\(_2\):MCl\(_2\) ratios during the formulation of the dispersions, the best trade-off between beneficial and detrimental doping-induced effects for HER may be achieved that the HER-activity of the ex-MoSe\(_2\):MCl\(_2\) flakes can be boosted further.

Concerning the heterostructures’ design (i.e., the design of SWCNTs/ex-MoSe\(_2\):MCl\(_2\)), the corresponding enhancement of the ex-MoSe\(_2\) HER-activity is rationalized by the electrochemical coupling that is established between SWCNTs and MoSe\(_2\) (Figure 6e), as causes a decrease in the \(\Delta G^0\) of the ex-MoSe\(_2\) flakes, as has been demonstrated by theoretical studies on carbon-based material/TMD hybrids.\(^{[89,90]}\) It is worth noting that the electrochemical coupling in heterostructures is preserved over a larger spatial range (i.e., \(\mu m\) scale) than that of hybrid compounds,\(^{[28-31,89,90]}\) as has recently been observed in our previous experimental works.\(^{[87,88]}\) In addition, different from the case of carbon-based nanomaterial/TMD hybrids, the heterostructured-based approach for designing HER-electrocatalysts permits each nanomaterial composing the overall electrocatalytic heterostructure to be independently processed. This simplifies the optimization of the material exfoliation protocol and ink formulation. Moreover, it is noteworthy that the use of SWCNT paper as a substrate eliminates the implementation of an electrocatalytic film transfer on rigid conductive current collectors (i.e., glassy carbon or metal-based substrates),\(^{[122]}\) which have to fulfill the electrochemical stability requirements.

3. Conclusion

In this work, we have demonstrated that the MCl\(_2\)-doping of ex-MoSe\(_2\) (i.e., the production of doped-MoSe\(_2\) nanoflakes/3d metal oxide–hydr(oxy)oxides hybrids) and the design of heterostructures between SWCNTs and ex-MoSe\(_2\):MCl\(_2\) are effective techniques with regard to designing pH-universal HER-electrocatalysts. In particular, the use of ex-MoSe\(_2\) produced by the cost-effective LPE of the bulk counterpart in an environmentally friendly solvent (i.e., IPA), the MCl\(_2\)-chemical doping and a solution-processed manufacturing of the heterostructured electrodes, manage to fulfill the key-requirements for pH-universal large-scale H\(_2\) production. In fact, the as-produced electrodes reached low \(\eta_0\) of 0.081 V and 0.064 V in 0.5 M H\(_2\)SO\(_4\) and 1 M KOH, respectively. The optimization of the heterostructure design (e.g., the material mass loading and layer thickness), heterostructure-stacking (e.g., the number of heterostructures) and MCl\(_2\)-doping (e.g., the ex-MoSe\(_2\):MCl\(_2\) molar ratio of the ex-MoSe\(_2\):MCl\(_2\) dispersion and the MCl\(_2\)-doping of SWCNT paper) are expected to further enhance the HER-performance herein achieved. Prospectively, our strategy to hybridize 3d metal oxide–hydr(oxy)oxide with HER-active electrocatalysts for enhancing the electrochemical performance of the native materials could be effective also for other HER-active low-dimensional materials beyond MoSe\(_2\), including metal oxides/\(\beta\)-phosphides,\(^{[131,132]}\)/carbides,\(^{[133,134]}\)/nitrides,\(^{[134,135]}\) as well as other TMDs.\(^{[5,136,137]}\) Therefore, we believe that our technology provides an effective low-cost alternative to the current state-of-the-art electrocatalytic production of H\(_2\) in both acidic and alkaline media.

4. Experimental Section

Synthesis of Materials: The ex-MoSe\(_2\) was produced by LPE,\(^{[44,45]}\) followed by SBS,\(^{[48-50]}\) in IPA of MoSe\(_2\) bulk (crystal, 99.995%, Sigma-Aldrich). In short, 30 mg of MoSe\(_2\) bulk were added to 50 mL of IPA and ultrasonicated in a bath sonicator (Branson 5800 cleaner, Branson Ultrasonics) for 6 h. The resulting dispersion was ultracentrifuged at 2700 g (Optima XE-90 with a SW32Ti rotor, Beckman Coulter) for 60 min at 15 °C in order to separate unexfoliated bulk MoSe\(_2\) (collected as sediment) from the ex-MoSe\(_2\) that remained in the supernatant. Then, the 80% of the supernatant was collected by pipetting, obtaining an ex-MoSe\(_2\) dispersion. The concentration of this ex-MoSe\(_2\) dispersion was adjusted to 0.4 g L\(^{-1}\) by evaporating any excess of the solvent.

The ex-MoSe\(_2\):MCl\(_2\) dispersions were prepared by dissolving MCl\(_2\) (FeCl\(_2\): anhydrous, 99.99% trace metals basis, Sigma-Aldrich; CoCl\(_2\): anhydrous, 99.99%, Sigma-Aldrich; NiCl\(_2\): anhydrous, 99.99%, Sigma-Aldrich; CuCl\(_2\): anhydrous, 99.99%, Sigma-Aldrich; ZnCl\(_2\): anhydrous, 99.99%, Sigma-Aldrich; CdCl\(_2\): anhydrous, 99.99%, Sigma-Aldrich) in the as-obtained ex-MoSe\(_2\) dispersion in IPA (ex-MoSe\(_2\):MCl\(_2\) molar ratio = 1:1). The resulting dispersions were sonicated in a bath sonicator (Branson 5800 cleaner, Branson Ultrasonics) for 30 min.

The SWCNTs (>90% purity, Cheap Tubes) were used as-received, without any purification step. The SWCNT dispersions were produced by dispersing SWCNTs in NMP at a concentration of 0.2 g L\(^{-1}\) and using ultrasonication-based debundling.\(^{[138-140]}\) Briefly, 10 mg of SWNT powder was added to 50 mL of IPA in a 100 mL open top, flat-bottomed beaker. The dispersion was sonicated using a horn probe sonic tip (Vibra-cell 75185, Sonics) with a vibration amplitude set to 45% and a sonication time of 30 min. The sonic tip was pulsed for 5 s on and 2 s off to avoid damage to the processor and to reduce any solvent heating. An ice bath around the beaker was used during sonication in order to minimize any heating effects.

The Pt/C powder (20 wt% platinum on carbon black, Alfa Aesar) was used as-purchased. The Pt/C dispersion was prepared by
dispersing Pt/C powder in 1 mL water/ethanol mixed solvent (v/v = 1:1) at a concentration of 5 mg mL⁻¹. Then, 10 μL of Nafion 117 solution (=5% in a mixture of lower aliphatic alcohols and water, Sigma-Aldrich) were added into the Pt/C dispersion. The so-obtained dispersion was sonicated for 30 min before the use.

**Characterization of Materials:** Transmission electron microscopy images were taken with a JEM 1011 (JEOL) transmission electron microscope, operating at 100 kV. Morphological and statistical analysis was carried out by using ImageJ software (NIH) and OriginPro 9.1 software (OriginLab), respectively. Samples for the TEM measurements were prepared by drop-casting the ex-MoSe₂ dispersion onto carbon-coated Cu grids, rinsing them with deionized water and subsequently drying them under vacuum overnight.

Atomic force microscopy images were taken using a Nanowizard III (JPK Instruments, Germany) mounted on an Axio Observer D1 (Carl Zeiss, Germany) inverted optical microscope. The AFM measurements were carried out by using PPP-NCHR cantilevers (Nanosensors, USA) with a nominal tip diameter of 10 nm. A drive frequency of ~295 kHz was used. Intermittent contact mode AFM images (512 x 512 data points) of 2.5 x 2.5 μm² and 500 x 500 nm² were collected by keeping the working set point above 70% of the free oscillation amplitude. The scan rate for the acquisition of images was 0.7 Hz. Height profiles were processed by using the JPK Data Processing software (JPK Instruments, Germany) and the data were analyzed with OriginPro 9.1 software. Statistical analysis was carried out by means of Origin 9.1 software on four different AFM images for each sample. The samples were prepared by drop-casting ex-MoSe₂ dispersions onto mica sheets (G250-1, Agar Scientific Ltd., Essex, U.K.) and drying them under vacuum.

X-ray photoelectron spectroscopy characterization was carried out on a Kratos Axis Ultra DLD spectrometer, using a monochromatic Al Kα source (15 kV, 20 mA). The spectra were taken on a 300 x 700 μm² area. Wide scans were collected with constant pass energy of 160 eV and an energy step of 1 eV. High-resolution spectra were acquired at constant pass energy of 10 eV and an energy step of 0.1 eV. The binding energy scale was referenced to the C 1s peak at 284.8 eV. The spectra were analyzed using CasaXPS software (version 2.3.17). The fitting of the spectra was performed by using a linear background and Voigt profiles. The samples were prepared by drop-casting ex-MoS₂ and ex-MoSe₂:MCl₂ dispersions on to a Si/SiO₂ substrate (LDB Technologies Ltd) and drying them under vacuum.

Raman spectroscopy measurements were carried out using a Renishaw microRaman i1000 with a 50x objective, an excitation wavelength of 532 nm and an incident power on the samples of 1 mW. For each sample, 50 spectra were collected. The samples were prepared by drop casting ex-MoS₂ and ex-MoSe₂:MCl₂ dispersions on Si/SiO₂ substrates and drying them under vacuum. The spectra were fitted with Lorentzian functions. Statistical analysis was carried out by means of OriginPro 9.1 software.

Van der Waals resistivity measurement was acquired on ex-MoSe₂ and ex-MoSe₂:NiCl₂ films with an average thickness of ~1.1 μm (mass loading of 0.8 mg cm⁻²). The material films were obtained by dropcasting the materials dispersions onto glass substrates. Metal contacts in van der Waals geometry were made with Ag paste, and current–voltage curves were measured with a Keithley 2600 SMU.

**Fabrication of Electrodes:** The ex-MoSe₂ and ex-MoSe₂:NiCl₂ were deposited on GC sheets (Sigma-Aldrich) (electrodes labeled ex-MoS₂ and ex-MoSe₂:MCl₂) by drop-casting the as-produced ex dispersion (mass loading of 0.2 mg cm⁻² referred to ex-MoS₂). The SWCNTs/ex-MoS₂ (or SWCNTs/ex-MoSe₂:MCl₂) were fabricated by depositing the SWCNT and ex-MoS₂ (or ex-MoSe₂:MCl₂) dispersion onto nylon membranes (Whatman membrane filters nylon, 0.2 μm pore size, Sigma-Aldrich) via a vacuum filtration process. The loading of the materials was 0.64 mg cm⁻² for both SWCNTs and ex-MoS₂ (for ex-MoSe₂:MCl₂ this value refers to the ex-MoSe₂). The electrode area was 3.14 cm². The Pt/C electrodes were realized by depositing Pt/C dispersion on GC sheets (mass loading of 0.35 mg cm⁻²). All the electrodes were dried overnight at room temperature before their electrochemical characterization.

Characterization of Electrodes: Scanning electron microscopy analysis was performed with a field-emission scanning electron microscope (Jeol JSM-7500 FA). The acceleration voltage was set to 5 kV. Images were collected using a secondary electron sensor for LEI images and the in-lens sensor for SEI images. Energy-dispersive X-ray spectroscopy images were acquired at 5 kV by a silicon drift detector (Oxford Instruments X-max 80) having an 80 mm² window. The EDX analysis was performed using Oxford Instrument AZtec 3.1 software. The SWCNTs/ex-MoSe₂:MCl₂ with M = Ni, Co, and Cd were analyzed as representative cases.

Electrochemical measurements were carried out at room temperature in a flat-bottom fused silica cell under a three-electrode configuration using CompactStat potentiostat/galvanostat station (iVium), controlled via iVium’s own iViumSoft. A Pt wire was used as the counter-electrode and saturated KCl Ag/AgCl was used as the reference electrode. Measurements were carried out in 200 mL of 0.5 M H₂SO₄ (99.999% purity, Sigma-Aldrich) or 1 M KOH (~85% purity, ACS reagent, pellets, Sigma-Aldrich). Oxygen was purged from the electrolyte by flowing N₂ gas through the liquid volume using a porous frit for 30 min before starting the measurements. A constant N₂ flow was maintained afterward for the whole duration of the experiments, to avoid the re-dissolution of molecular oxygen in the electrolyte. The potential difference between the working electrode and the Ag/AgCl reference electrode using the RHE scale was converted to the RHE scale via the Nerst equation: $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197 V$. In which $E_{RHE}$ is the converted potential versus RHE, $E_{Ag/AgCl}$ is the experimental potential measured against the Ag/AgCl reference electrode, and $E_{Ag/AgCl}$ is the standard potential of Ag/AgCl at 25 °C (0.1976 V vs RHE). The LSV curves were acquired at the scan rate of 5 mV s⁻¹. Polarization curves from all catalysts were iR-corrected, in which i is the measured working electrode current and the R is the series resistance that arises from the working electrode substrate and electrolyte resistances. R was measured by electrochemical impedance spectroscopy at open-circuit potential and at the frequency of 10⁴ Hz.

The linear portions of the Tafel plots fitted the Tafel equation $\eta = b \log (\frac{|j|}{a}) + A$ ([85,142]), in which $\eta$ is the overpotential in comparison with the reversible hydrogen electrode potential (0 V vs RHE), j is the current density, b is the Tafel slope and A is the intercept of the linear regression. By setting $\eta$ equal to zero in the Tafel equation, the j₀ was calculated. Stability tests were carried out by chronoamperometry measurements (j-t curves), i.e., by measuring the current in the potentiostatic mode at a fixed overpotential of 0.25 V for ex-MoSe₂:MCl₂ (GC substrate) and 0.18 V for SWCNTs/ex-MoSe₂:MCl₂ (heterostructure) in 5 M H₂SO₄ over time.

Elemental analysis by inductively coupled plasma optical emission spectroscopy was performed with a Thermo Fisher ICAP 6000 Duo inductively coupled plasma optical emission spectrometer. The samples were digested solutions prepared from the 0.5 M H₂SO₄ solutions (volume of 100 mL) recovered after carrying out the HER measurements of SWCNTs/ex-MoSe₂:CdCl₂ or SWCNTs/ex-MoSe₂:NiCl₂. To avoid incompatibilities of the ICP-OES system with the presence of H₂SO₄, the aliquot (3 mL) used for the analysis was neutralized to pH = 7 using NH₄OH (5 M, Fluka, 120 μL). Following this procedure, no metals were added in the solution. This was confirmed by the blank prepared just using water and the same amount of NH₄OH solution. Then, two series of samples together with the corresponding blank were prepared in a 25 mL volumetric flask, digesting the neutralized aliquot in 2 mL of aqua regia (HCl:HNO₃, volume ratio of 3:1) overnight and 2 days, respectively. Prior to the measurement, each sample was diluted by 25 mL with Millipore water to the total volume, and stirred by vortex at 2400 rpm for 10 s. Lastly, the sample was filtered using a PTFE membrane (0.45 μm pore size). Three measurements were performed on each sample to obtain the final averaged values of metal concentration.

**Supporting Information**

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

L.N. and S.B. contributed equally to this work. This project has received funding from the European Union’s Horizon 2020 research and innovation program under Grant Agreement No. 785219—GrapheneCore2. The authors thank Beatriz Martín-García for her support in ICP-MS measurements; Lea Pasquale (Materials Characterization Facility, Istituto Italiano di Tecnologia) for her support in XPS data acquisition; Electron Microscopy facility, Istituto Italiano di Tecnologia for support in SEM/TEM data acquisition; Davide Spirito for his support in van der Pauw resistivity measurements; Nanochemistry Characterization Facility, Istituto Italiano di Tecnologia) for her support in ICP-MS measurements; Lea Pasquale (Materials GrapheneCore2. The authors thank Beatriz Martín-García for

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, electrocatalysts, hydrogen evolution reaction (HER), molybdenum diselenide (MoSe2), transition metal dichalcogenides (TMDs)

Received: June 6, 2018
Revised: July 4, 2018
Published online: August 8, 2018
