



Interfacial Mn-Ni selenide/ $\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene heterostructures for integrated water splitting and supercapacitive energy storage

Arunachala Kumar S.P.^{a,e}, Senthilkumar Ramasamy^b, Narendhar Chandrasekar^{c,*},
Saradh Prasad Rajendra^d, Khalid Eidah Alzhrani^d, Seung Jun Lee^{e,*},
Subramania Angaiah^{a,e,*}

^a Electro-Materials Research Laboratory, Centre for Nanoscience and Technology, Pondicherry University, Puducherry 605014, India

^b Center of Excellence in Advanced Materials and Green Technologies, Amrita School of Engineering, Amrita Vishwa Vidyapeetham University, Coimbatore 641112, India

^c Department of BioNanoTechnology, Gachon University, Sujeong-Gu, Seongnam-si 13120, Republic of Korea

^d Research Chair for Laser Diagnosis of Cancers, Department of Physics and Astronomy, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

^e Department of IT-Energy Convergence (BK21 Four), Korea National University of Transportation, Chungju 27469, Republic of Korea

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ABSTRACT

Green hydrogen production via electrocatalytic water splitting offers a sustainable pathway toward zero-carbon energy systems. However, sluggish charge-transfer kinetics, poor stability, and high costs of electrocatalysts limit practical applications. To address these challenges, we anchor a manganese - nickel (Mn-Ni) selenide onto $\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene via a solvothermal approach, integrating MXene's intrinsic conductivity with the redox-active Mn/Ni sites. The resulting hybrid exhibits excellent bifunctional activity, achieving 10 mA cm^{-2} at low overpotentials of 173 and 232 mV for HER and OER, respectively, outperforming RuO_2 . The full water-splitting cell reaches 100 mA cm^{-2} at 1.74 V while demonstrating robust durability over 100 h. Beyond electrocatalysis, as a supercapacitor electrode, the hybrid delivers a high specific capacitance of 2106 F g^{-1} at 1 A g^{-1} , and the symmetric device achieves an energy density of 43.4 Wh kg^{-1} at 750 W kg^{-1} , highlighting its exceptional energy storage performance. This study provides a rational strategy for designing bimetallic MXene-selenide hybrid heterostructures as multifunctional materials for integrated energy conversion and storage applications.

1. Introduction

Growing energy demands, depletion of fossil fuels, and escalating environmental concerns have prompted global efforts to transition toward clean and sustainable energy sources. Hydrogen (H_2) has emerged as a promising alternative owing to its high energy density (142 MJ kg^{-1}) and pollution-free, carbon-neutral emission profile [1,2]. Among various hydrogen production technologies, electrocatalytic water splitting has gained significant attention as an attractive and scalable approach due to its environmentally benign and sustainable nature. However, the water electrolysis contributes 4% of global H_2 production, while > 90% remains derived from carbon-intensive techniques like steam methane reforming and coal gasification [3–5]. In general, the overall water splitting comprises two half reactions: the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution

reaction (OER). The kinetics of HER are favourable in an acidic environment, but are plagued by corrosion. Whereas in alkaline media, the pathway is hindered by sluggish water dissociation, limiting its efficiency [6,7]. Meanwhile, OER, a four-proton-coupled electron transfer involving $\ast\text{O}$, $\ast\text{OH}$, $\ast\text{OOH}$ intermediates, necessitates higher overpotentials. Although Platinum group metal (PGM) and Ir/Ru oxides are benchmark HER and OER electrocatalysts, the natural scarcity, limited durability, and high cost hamper their large-scale industrial operation [8,9]. These issues made intensive exploration and exploitation of the earth-abundant, non-noble bifunctional electrocatalyst for water splitting.

Transition metal-based compounds belonging to groups IV–VII—such as oxides, sulfides, carbides/nitrides, and phosphides, etc., have been extensively investigated as bifunctional electrocatalysts for water splitting owing to their low cost, adjustable catalytic properties,

* Corresponding authors.

** Corresponding author at: Electro-Materials Research Laboratory, Centre for Nanoscience and Technology, Pondicherry University, Puducherry 605014, India.

E-mail addresses: narendhar.nano@gmail.com (N. Chandrasekar), sjlee@ut.ac.kr (S.J. Lee), a.subramania@gmail.com (S. Angaiah).

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tunable electronic structures and wide availability [10–12]. Among them, transition metal selenides have attracted particular attention owing to their versatile compositions and unique physicochemical properties, which can be further optimized through atomic-level modification and structural engineering [13,14]. Among them, Nickel (Ni)-based selenides are the most promising, as Ni possesses favorable electrochemical activity, tunable band structures, and multiple oxidation states close to oxygen reduction potential, showing better catalytic performances [15–17]. For instance, a strategy was demonstrated to enhance the performance of the electrocatalyst by Fe-doping into NiSe/Ni₃Se₂ heterojunction, which exhibits an enhanced catalytic activity and stability over 100 h [18,19]. Similarly, the NiSe₂/NiS heterostructures fabricated by a one-pot hydrothermal process, proving that modulating the d-band energy center delivers an exceptional catalytic performance [20]. An amorphous-crystalline interfaces in the MOF-assisted Fe_{0.4}Ni_{0.6}Se₂ and NiS₂ modulates the electronic structure, resulting in efficient HER and OER [21]. Similarly, introduction of copper into NiSe₂ markedly reduces the overpotential values of HER (316 mV) and OER (248 mV) along with Tafel values [22]. And the Insitu grown multimetallic catalyst also shows better performances with a low cell voltage of 1.7 V to reach 100 mA cm⁻², showcasing its advantages of different band center [23]. While these advancements illustrate that compositional and interfacial engineering can enhance HER/OER performance and maintain stability, but unable to address the challenges of low conductivity and active site dispersions, remaining critical for industrial applications [24].

A persistent limitation of Ni-based selenides is their low metal d-band center, which obstructs the adsorption of the reaction intermediates and constrains their intrinsic efficacy. Atomic-level modification through the incorporation of secondary metals (such as Fe, Co, or Mn) can induce localized lattice polarization, enhance intermediate adsorption, and promote the formation of active metal hydroxides/oxides via d–p orbital hybridization [15,16,25]. In addition, tuning the electronic state and constructing an amorphous structure improves the reaction kinetics, accelerates charge transfer, and deepens electronic potential wells, thereby augmenting the density of active sites [26]. Despite these advances, the bifunctional catalytic properties remain unsatisfied due to the adsorption capacity of the reaction intermediates. Specifically, the HER intermediates (H⁺) absorb at nucleophilic sites, and the OER intermediates (OH⁻) at electrophilic sites, making it challenging to design a single TMSe catalyst with dual functionality. Therefore, constructing a heterogeneous interface that integrates both types of active sites is a promising strategy. Such an interface can introduce distinct energy levels and enhance the interfacial electric field, thereby finely tuning the electronic structure and optimizing the overall catalytic activity [27].

As an emerging 2D material, MXene has garnered enormous interest owing to its inherent physicochemical characteristics, high electrical conductivity ($\approx 9880 \text{ S cm}^{-1}$), abundant active sites, strong hydrophilicity and rich surface functional groups (-OH, -O, and -F) [28–31]. However, pristine Ti-based MXenes have shown remarkable HER performance in acidic media, but demonstrate subpar HER/OER performances in alkaline media, due to the surface oxidation and unfavorable surface chemistry [32,33]. In contrast, MXene-supported electrocatalysts exhibit significantly enhanced catalytic performance, ascribed to their enhanced structural stability, excellent electrical conductivity, and accelerated redox kinetics [34]. These enhancements arise from the strong synergistic interactions between the catalytically active species and the conductive MXene substrate [35,36]. Specifically, in TMSe, the MXene acts as an effective anchor, preventing aggregation, facilitating rapid electron transfer, regulating charge distribution and optimizing the formation of electrophilic/nucleophilic sites. For example, a novel NiSe₂@MXene/rGO aerogel with a cellular lattice-like network increases the electrode-electrolyte contact area, boosting the mass diffusion rate, electrical conductivity, and charge transport [37]. Similarly, the electronic coupling between NiFeS and MXene sheets of the

NiFeS@MXene electrocatalyst optimizes the adsorption energies of intermediates, resulting in enhanced bifunctional catalytic activity [38]. In another approach, the coupled Ni-MoSe₂ with Ti₂N_{T_x} MXene combines the MXene's conductive substrate and rich MoSe₂ active sites. And the addition of Ni to the Mo-Se system alters the electronic d-band center, optimizing reaction intermediates and improving durability [39].

Recent studies involving MXene-based transition-metal composites show much better performance due to an advanced understanding of interfacial chemistry and the utilisation of their synergistic effects. The integrated CoSe with Ti-MXene exhibits better HER activity in both fresh and saline water, with a low overpotential of -299 mV [40]. Similarly, hierarchical CoSe₂/TiSe₂@Ti₃C₂T_x MXene developed by in situ selenization provides better OER and supercapacitor performances [41]. The interfacial phase engineering establishes strong electronic coupling, promoting fast electron transfer, structural stability and enhanced redox kinetics. The rationally designed Mn₃O₄/CuO/MXenes demonstrate superior performance results from limited aggregation, better charge transfer rate, and more active sites, resulting in 12 hrs of stability [42]. In the latest study of atomic-scale confinement of Pt by Se-Ti-MXene, it activates strong metal bonding with favourable electronic and geometrical configurations, synergistically affecting the internal electronic structure optimization and external spatial configuration. Thus, it exhibits a low overpotential of 54 mV in the alkaline media [43].

Despite recent progress, several challenges associated with MXene-TMSe composites, including weak physical adsorption, imbalanced bifunctional performance, arise from mismatched adsorption energies of H⁺ and OH^{*} intermediates, and structural instability, arising from surface oxidation and nanoparticle agglomeration, leading to poor durability under long-term operation. These issues can be addressed by applying mixed-metal MXenes with secondary transition metals (Nb, V, Mo, etc), contributing additional electronic modification arising from the presence of another metal layer within the carbide layers. The application of mixed-metal MXenes, such as Ti₂NbC₂T_x, offers additional electronic modulation via the secondary metal layer, enhancing active-site density. However, the mechanistic understanding of these modifications and their effect on bifunctional electrocatalysis is still limited. To address these limitations, integrating TMSe with double metal MXene is expected to generate a unique heterostructure, promoting enhanced interfacial charge transfer and improved electrochemical performance. Further, acknowledge our previous work on CoNi₂Se₄@TiNb-MXene and clearly distinguish the novelty of the present study [44,45]. The key advancement lies in the substitution of Co with Mn, which introduces distinct electronic characteristics due to its multiple oxidation states, enabling effective tuning of the electronic structure and catalytic behavior. In addition, XPS analysis reveals site-selective charge redistribution and strong interfacial interactions, consistent with possible Se–O–MXene-type bonding, indicating stronger coupling compared to simple physical mixing. Furthermore, the present system has been evaluated under extended operational conditions (up to 100 mA cm⁻² with long-term stability) and demonstrates multifunctionality for both water splitting and supercapacitor applications. Overall, this work provides deeper insight into Mn-based MXene-selenide systems, featuring enhanced interfacial coupling and broader performance validation compared to our previous study [34].

Herein, we report the rational design of MnNi₂Se₄/Ti₂NbC₂T_x MXene hybrid structure using a 2-step solvothermal technique as a bifunctional electrocatalyst for water splitting. Compared to monometallic selenides, bimetallic selenides offer greater flexibility in tuning the electronic d-band centre, promoting catalytic activity through synergistic interactions, thereby optimizing the adsorption energies of the reaction intermediates. In this designed heterostructure, Ni provides primary catalytic active sites, while Mn modulates the electronic structure, Se enhances conductivity, and TiNb-MXene offers conductive surfaces with abundant active sites. The nanoparticle/nanoplate architecture suppresses MXene restacking and MnNi₂Se₄ aggregation, facilitates charge

transfer, and improves durability. Beyond electrocatalysis, this hybrid is also demonstrated as a high-performance supercapacitor electrode, leveraging Mn's redox activity and MXene's intrinsic conductivity, thereby achieving integrated material-level multifunctionality. The unique multi-interfacial engineering, boost HER/OER performances and deliver low cell voltage with excellent durability. Thus, this study develops a cost-effective, robust multifunctional material for both a sustainable energy conversion (electrocatalyst for water splitting) and an advanced energy storage system (electrode material for supercapacitor applications).

2. Experimental section

$\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene (TiNb-MXene) was synthesized by selectively etching the Al layer from the $\text{Ti}_2\text{NbAlC}_2$ MAX phase [46–48]. 1.0 g of MAX phase powder was added to 40% hydrofluoric acid (HF) in a 1:20 (g mL^{-1}) solid-to-liquid ratio (MAX:HF), and the mixture was stirred continuously at 350 rpm and 70°C for 55 h. The resulting suspension was repeatedly washed with deionized (DI) water (typically 5–7 times) until a neutral pH (~ 6 – 7) was achieved. The solution was then vacuum-filtered using filter paper ($0.22\ \mu\text{m}$), followed by drying in a vacuum oven at 60°C for 24 h to obtain a few-layered TiNb-MXene nanosheets, which were finally collected and stored under a vacuum desiccator to minimize surface oxidation for future use. HF is highly corrosive and toxic, and all the etching processes were carried out in a fume hood using Teflon containers.

The MnNi_2Se_4 -decorated $\text{Ti}_2\text{NbC}_2\text{T}_x$ -MXene (MNS@TiNb-MXene) hybrid electrode was synthesized via a two-step solvothermal method using *N,N*-dimethylformamide (DMF) as the solvent. Initially, 100 mg of the TiNb-MXene was dispersed in 100 mL of DMF using bath sonication for 30 min, followed by 2 h of magnetic stirring to ensure uniform dispersion. Subsequently, $\text{Mn}(\text{NO}_3)_3$ (0.5 mmol), $\text{Ni}(\text{NO}_3)_2$ (1 mmol) and urea (5 mmol) were added in a 1:2:10 molar ratio under continuous stirring to form a homogeneous precursor solution. The 1:2 molar ratio of Mn and Ni corresponds to stoichiometric composition, and the excess of urea facilitates controlled hydrolysis and nucleation. The resultant solution was stirred for an additional 2 h, then transferred into a Teflon-lined stainless-steel autoclave and heated at 130°C for 16 h. After cooling to room temperature, the final product was collected by centrifugation, thoroughly washed with DI water, and dried in a vacuum oven at 60°C overnight. In the second step, Na_2SeO_3 (10:1 molar ratio) was dissolved in 100 mL of DMF and stirred for 20–30 min. Subsequently, 5 mL of hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) was slowly added under continuous stirring for 30 min. The previously prepared Mn-Ni hydroxide intermediate was then added to the above mixture and stirred for 2 h at room temperature, followed by transfer to a Teflon-lined stainless-steel autoclave. The autoclave was heated at 180°C for 8 h. After cooling to room temperature, the final product was collected by centrifugation, washed, and dried in a vacuum oven at 60°C overnight. The synthesized hybrid electrode material was stored under vacuum and denoted as MNS@TiNb-MXene . For comparison, MnNi_2Se_4 nanoparticles (MNS) were synthesized following the same procedure without the addition of TiNb-MXene .

The material characterization, electrode fabrication and the electrochemical measurement were discussed in the [supporting information](#).

3. Results and discussion

The preparation of MNS@TiNb-MXene is schematically elucidated in Scheme 1. The layered TiNb-MXene prepared by etching Al from the $\text{Ti}_2\text{NbAlC}_2$ MAX phase, leaving dense surface termination groups generally -F, -O, and -OH. Upon washing with DI water, the -F termination group was gradually replaced by -OH and -O groups, increasing surface reactivity and hydrophilicity [49,50]. In the first step of the solvothermal process, cations, such as Ni and Mn, were electrostatically attracted to the MXene nanosheets due to their negative surface energy.

The presence of urea prevents the agglomeration, controls the nucleation and growth of cations over the TiNb-MXene sheets, forming a unique hierarchical structure with exposed active sites. In the subsequent process, sodium selenite was used as a Se precursor and hydrazine hydrate was used to reduce Se into anionic Se (Se^{2-}) [51]. After adding the intermediates into the above mixture, the anionic Se reacts with the intermediates under solvothermal conditions, leading to the uniform decoration of Mn-Ni-Se nanoparticles over the surface of TiNb-MXene .

3.1. XRD studies

X-ray diffraction studies were conducted to investigate the crystal structure of the prepared MnNi_2Se_4 , and the obtained pattern is shown in Fig. 1a and Figure S2. The observed diffraction peaks at the 2θ values of 27.72° , 29.76° , 31.34° , 33.46° , 36.76° , 42.84° , 45.36° , 46.70° , 50.52° , 55.40° , and 57.56° are close to, but slightly shifted from, the cubic crystal system of MnSe and NiSe [52,53]. Critically, the obtained pattern is distinctly different from the diffraction peaks of both the monometallic selenides, MnSe (JCPDS #98-009-0058) and NiSe (JCPDS #98-002-3840) phases. The observed peaks shift, particularly at 29.76° , 33.46° , and 36.76° , compared to NiSe (29.94° , 33.58° , 36.89°), suggesting that Mn incorporation into the NiSe framework induces lattice expansion and distortion. These systematic shifts are consistent with intermediate lattice distortion attributed to the difference in ionic radii of Mn^{2+} ($0.83\ \text{\AA}$) and Ni^{2+} ($0.69\ \text{\AA}$), and likely from the interfacial interaction. The absence of strong individual binary peaks of MnSe and NiSe and the systematic peak shifts suggest the formation of bimetal selenide rather than a physical mixture, consistent with the successful synthesis of MnNi_2Se_4 .

The XRD pattern of the composite MNS@TiNb-MXene exhibits the characteristic peaks of both the crystalline TiNb-MXene and MnNi_2Se_4 . The (002) reflection of the MXene at 2θ values of 6.5° indicates the structural stability during the synthesis process, and the peaks of MnNi_2Se_4 in the composite are consistent with those observed in the pristine selenide pattern. The slightly broadened peaks of MnNi_2Se_4 are consistent with reduced crystallite size and possible strain induction by strong interfacial interaction with the MXene surface. These observations suggest the successful integration of MNS to the TiNb-MXene substrate [54,55]. Notably, no additional impurity peaks corresponding to secondary phases are observed within the detection limits of XRD, suggesting phase purity of the synthesized materials.

3.2. Raman studies

The vibrational mode analysis, performed using Raman spectroscopy, confirms the formation of the MnNi_2Se_4 phase, as shown in Fig. 1b. The spectrum exhibits the characteristic peaks at 271, 331, 535, 711 and $793\ \text{cm}^{-1}$, and is distinct from the binary phases MnSe (233.8 , $360\ \text{cm}^{-1}$) and NiSe (217 , $245\ \text{cm}^{-1}$) [56,57]. The main peak shifts to $271\ \text{cm}^{-1}$ from $245\ \text{cm}^{-1}$ (NiSe) and $331\ \text{cm}^{-1}$ from $360\ \text{cm}^{-1}$ (MnSe), indicating the altered local chemical environment due to the presence of shared Mn and Ni lattice, altering the vibrational frequencies. The appearance of a strong, dominant stretching vibration at $535\ \text{cm}^{-1}$ is the signature of long-range order in the Mn-Ni-Se lattice, and the peak broadening is ascribed to cation disorder between Mn and Ni in the crystal structure. The absence of strong binary features, the emergence of new high-frequency vibrations, continuous alterations and expansion of low-frequency modes signify a composite Mn/Ni local environment, the characteristic of a unique ternary phase, rather than a mere physical mixture of binaries. The Raman spectra of the composite MNS@TiNb-MXene provide the strong evidence for the successful synthesis and interfacial interaction between components (Fig. 1b). The disappearance of MXene's characteristic peaks at 260.3 and $362.7\ \text{cm}^{-1}$ may arise from multiple factors, including signal attenuation due to surface coverage by MnNi_2Se_4 , overlapping vibrational modes and reduced Raman scattering from the MXene layers. The appearance of

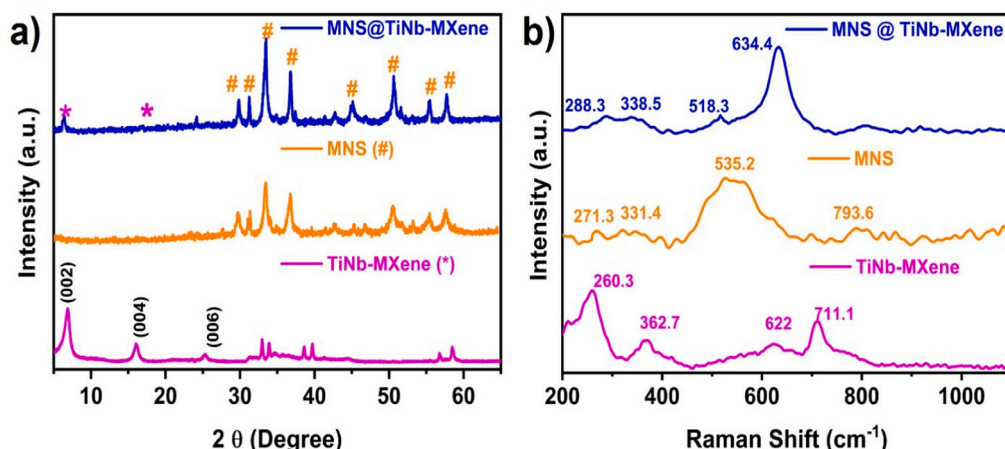


Fig. 1. a) XRD patterns and b) Raman spectra of the prepared $\text{Ti}_2\text{NbC}_2\text{T}_x$ (TiNb-MXene), MNS, and MNS@TiNb-MXene.

new peaks at 288 cm^{-1} suggests interfacial coupling between the MXene surface functional groups (-O/-OH) and selenide, likely forming interfacial Se-O-Ti/Nb vibrations, as corroborated by XPS analysis [58,59]. The distinct peaks at 338 and 518 cm^{-1} confirm the presence of the MnNi_2Se_4 phase on the MXene surface. Moreover, the carbon peak shift from 622 to 634 cm^{-1} confirms the strong electronic interaction and strain modulation between the MXene layer and anchored MnNi_2Se_4 , altering the local environment of the carbon atoms. Collectively, these Raman analyses, in concert with XPS and XRD evidence, validate the strong evidence for structural modification and interfacial interaction in successful formation of $\text{MnNi}_2\text{Se}_4/\text{MXene}$ heterostructure.

3.3. FESEM studies

The FESEM image of MNS at the micrometer scale (500 nm scale, magnification: $50\text{k} \times$) (Figure S2a) exhibits a large, plate-like agglomerate of fine and densely packed nanoparticles. The highly textured, visible sub-micron granular and porous nature resulted from the aggregation of smaller crystallites. On higher magnification (100 nm scale,

magnification: $200\text{k} \times$) (Figure S2b), the particle exhibits irregular, rough surfaces, a broad size distribution, with an interconnected, loosely aggregated structure, suggesting a high surface area and internal porosity favorable for catalytic applications. In contrast, the MNS@TiNb-MXene composite (Fig. 2a) displays MnNi_2Se_4 nanoparticles uniformly anchored on the MXene surface, forming a hierarchical sheet-like morphology covered with smaller granular particles (500 nm scale, magnification: $50\text{k} \times$). Fig. 2b sub-micron (100 nm scale, magnification: $200\text{k} \times$) image reveals the well-defined, faceted nanoplate-like MnNi_2Se_4 , integrated within a more open and less densely agglomerated framework, compared to pristine MNS. The uniform, nanoplate-like, controlled growth of MnNi_2Se_4 , facilitated by the MXene scaffold, minimizes aggregation, ensures higher dispersion, and enhances interfacial contact, thereby promoting efficient charge transfer and catalytic activity.

The elemental mapping of the MNS@TiNb-MXene composites confirms a homogenous distribution of Mn, Ni, Se, Ti, Nb, and C, evidencing uniform integration of MnNi_2Se_4 with the MXene substrate. The mapping contrast suggests the preferential coverage of MnNi_2Se_4 over the

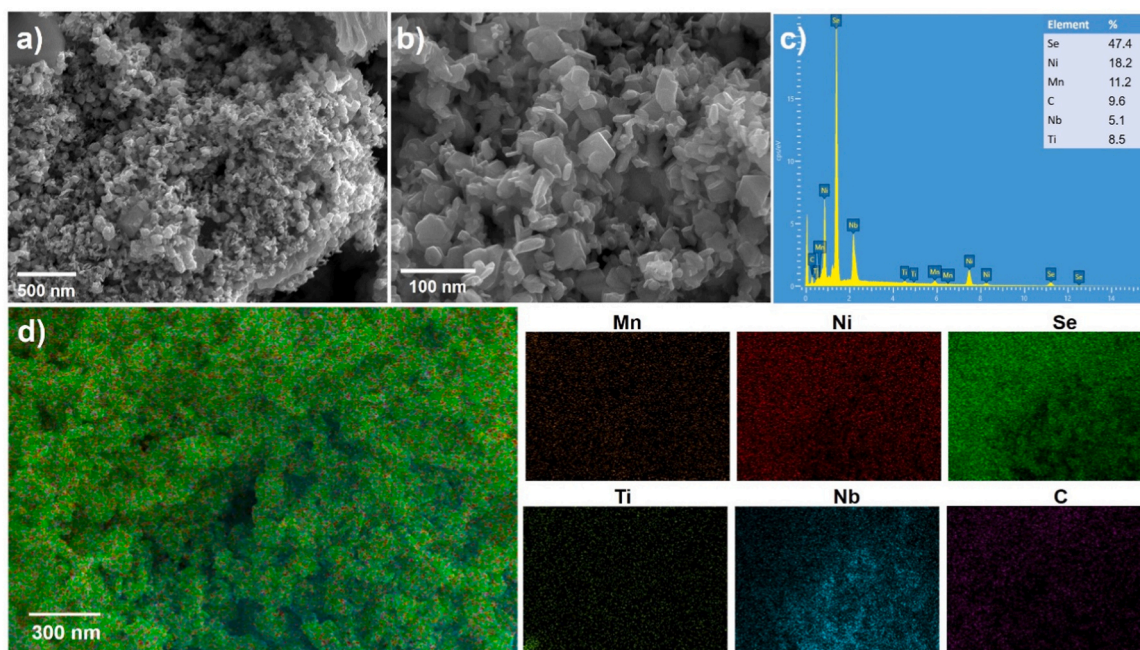


Fig. 2. a) FESEM image, b) Higher magnification, c) EDX spectrum, and d) elemental mapping of constituent elements in the prepared MNS@TiNb-MXene composite.

$\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene. This indicates the effective anchoring and intimate interfacial contact of MnNi_2Se_4 and TiNb-MXene . While the mapping suggests the surface coverage, the possible role of this MnNi_2Se_4 layer in suppressing surface oxidation (passivation effect), supported by XPS and the observed long-term electrochemical stability, rather than being inferred solely from imaging contrast. Further, the energy dispersive X-ray spectrum of MNS in Figure S1 shows the average atomic ratio of Mn/Ni/Se $\approx 16.5/27.2/56.3$ (± 0.7), obtained from multiple randomly selected regions. The ratio is close to the theoretical MnNi_2Se_4 stoichiometry, confirming the successful formation of the bimetallic selenide. The slight deviation in excess of Mn and deficit of Ni and Se could arise from surface enrichment, cation deficiency or anion vacancies, local inhomogeneity or the instrumental uncertainty. The composite EDX spectrum in Fig. 2c&d shows the presence of all the elements, with a higher concentration of surface MnNi_2Se_4 relative to the interior $\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene substrate, confirming the successful anchoring of the chalcogenide phase on the 2D MXene scaffolds.

3.4. XPS studies

The Mn 2p spectra (Fig. 3a) exhibit distinct peaks, indicating the presence of mixed oxidation states of Mn^{2+} and Mn^{3+} in the pristine MNS. The peak at 636.95 eV is attributed to the Mn^{2+} multiplet splitting resulting from Mn-Se bonding. The + 0.44 eV shifted peak at (640.86 eV to 641.3 eV) results from interfacial charge transfer from Mn to the TiNb-MXene , likely via Se-Mn-O-Ti/Nb bonds. And the peak at 644.04 eV is attributed to Mn^{3+} or Mn-O bonding with MXene terminations [58,60]. The Ni 2p spectra (Fig. 3b) show distinct Ni^{2+} and Ni^{3+} peaks in the spin-orbit doublets at 853.19 and 870.44 eV for Ni^{2+} and 854.62 and 872.94 eV for Ni^{3+} . The positive shifts at Ni^{2+} confirm the electron donation to TiNb-MXene , aligning with Mn 2p. The oxidized Ni^{3+} peaks suggest Ni-O-Ti/Nb bond formation at the hetero junction,

and the negative satellite peak shift (-0.59 eV) indicates reduced shake-up intensity, attributed to interfacial shielding from atmospheric contaminants by MXene [61]. Eventually, in the O 1s spectra (Fig. 3c), the peak at 531.64 eV, with higher intensity, arises from interfacial O-Mn/Ni-O bonds and modified -OH groups resulting from MnNi_2Se_4 interaction. The composite formation reduces the O-Ti bond and adsorbed water (533.03 eV $\rightarrow$ 532.96 eV) intensities, but increases the -OH/oxidized oxygen signal, implying interfacial reactions and surface passivation by physically covering MXene surfaces with MnNi_2Se_4 . In Se 3d deconvoluted spectra (Fig. 3d) exhibit two characteristic peaks at 54.65 and 55.59 eV assigned to spin-orbit doublet ($3d_{5/2}$ and $3d_{3/2}$) of Se^{2-} in the MnNi_2Se_4 and 58.65 eV attributed to surface oxidized Se species (SeO_x). In the composite, the positive peak shifts to higher BE, indicating a modification of the Se electronic structure due to charge transfer or interfacial electronic interaction with MXene. The new peak emergence at 57.33 eV BE, absent at MnNi_2Se_4 , was observed between the typical BE of the metal selenide (Se 3d) peak (~ 3 eV) and oxidized SeO_2 peak, reflecting a unique bonding environment, consistent with interfacial Se-O species. This feature is attributed to the possible interfacial Se-O bonding with the surface functional group of MXene (Se-O-MXene), indicative of electronic coupling and charge transfer at the heterointerface.

The satellite peak shift and reduced intensity observed in all deconvolution spectra suggest suppressed shake-up processes, suggesting interfacial shielding from atmospheric contaminants by MXene integration, which contributes to surface passivation. Compared to the pristine material, the deconvoluted spectra of Mn 2p, Ni 2p and Se 3d of the composite show positive shifts in the binding energies, indicating a decrease in local electron density. The shift suggests that the electron redistribution and strong electronic interaction result in electron withdrawal from MnNi_2Se_4 upon hybridization. The changes absorbed in the deconvoluted spectra of all constituent elements further confirm

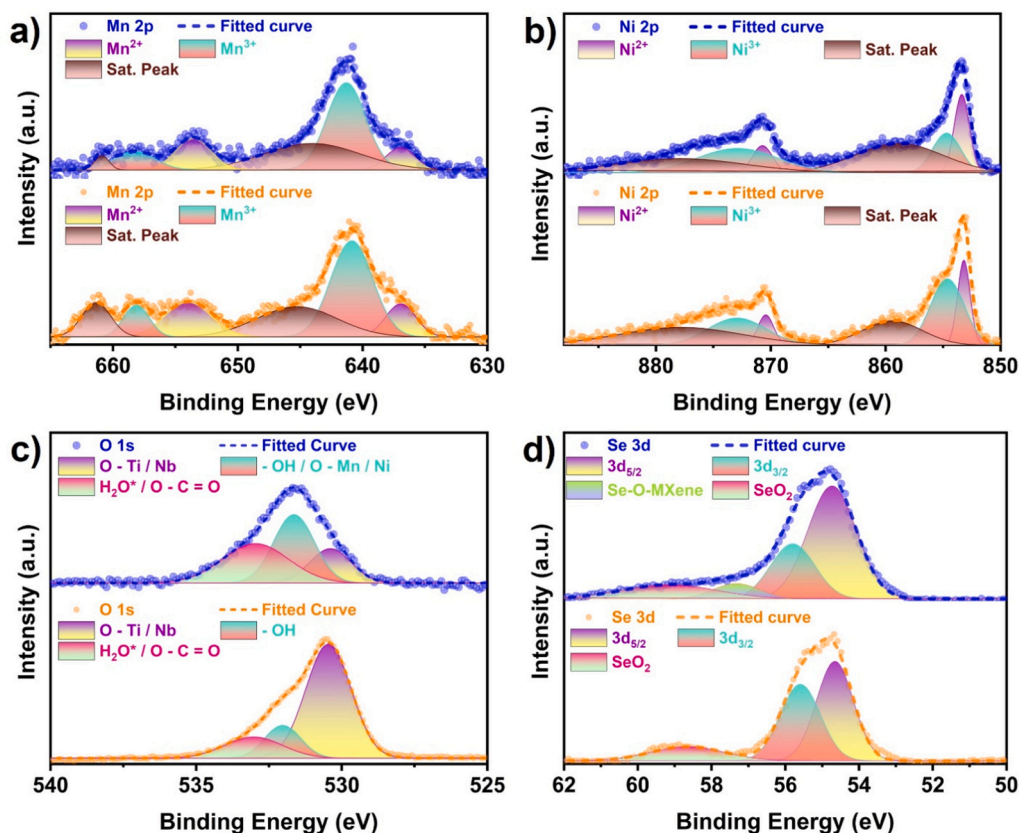


Fig. 3. Deconvoluted XPS Spectra of a) Mn 2p, b) Ni 2p, d) Se 3d (Top: MNS@TiNb-MXene, Bottom: MNS), and c) O 1s (Top: MNS@TiNb-MXene, Bottom: TiNb-MXene).

electronic coupling and strong interfacial interaction between MnNi_2Se_4 and $\text{Ti}_2\text{NbC}_2\text{T}_x$, involving charge redistribution and the formation of new chemical bonds, as well as enhanced surface passivation/oxidation induced by their mutual electronic coupling [61–64].

3.5. HRTEM analysis

To further investigate the morphology and microstructure of the prepared MNS and MNS@TiNb-MXene materials, TEM, HRTEM, and selected area electron diffraction (SAED) analyses were performed. Figure S4a–c shows the TEM, HRTEM images, and SAED pattern of MNS, respectively. The MNS nanoparticles exhibit a rectangular, plate-like morphology with relatively smooth edges, consistent with FESEM observations. The HRTEM image reveals clear lattice fringes with interplanar spacings of 0.237 nm and 0.189 nm, corresponding to the (220) and (311) planes of M_3X_4 -type chalcogenides. The SAED pattern displays concentric diffraction rings with discrete spots, indicating the polycrystalline nature of the material with randomly oriented nanocrystals. Fig. 4a presents the TEM image of the MNS@TiNb-MXene composite, showing that MnNi_2Se_4 nanoparticles are uniformly dispersed and closely anchored on the $\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene sheets, suggesting intimate interfacial contact and the formation of a heterostructure without noticeable aggregation. The HRTEM image (Fig. 4b) reveals two distinct lattice fringe spacings of ~ 0.17 nm and ~ 0.26 nm, attributed to $\text{Ti}_2\text{NbC}_2\text{T}_x$ MXene and MnNi_2Se_4 , respectively. The coexistence of these lattice fringes within the same region supports the formation of a well-integrated heterostructure with close interfacial proximity. The SAED pattern (Fig. 4c) shows superimposed diffraction features corresponding to both MXene and MnNi_2Se_4 phases, confirming their coexistence. No additional diffraction rings or spots corresponding to impurity phases are observed within the detection limit. Overall, the TEM analysis confirms the formation of a well-dispersed $\text{MnNi}_2\text{Se}_4/\text{Ti}_2\text{NbC}_2\text{T}_x$ heterostructure with intimate interfacial contact, which is consistent with the interfacial interaction inferred from XPS and Raman analyses.

3.6. Electrochemical studies

Linear sweep voltammetry studies were performed using a 3-electrode configuration to evaluate the HER electrocatalytic performance of the prepared electrocatalysts in 1 M KOH at a scan rate of 2 mV s^{-1} . The catalyst-coated nickel foam was used as the working electrode, with Ag/AgCl and a Pt wire serving as the reference and counter electrodes, respectively. The polarization curves, after being corrected with 90% iR compensation, are presented in Fig. 5a. The MNS and TiNb-MXene electrocatalysts showed an overpotential of 195 mV and 265 mV vs RHE, respectively, to achieve a current density of 10 mA cm^{-2} . In contrast, the MNS@TiNb-MXene composite required only 173 mV vs. RHE to reach the same current density, demonstrating a markedly superior HER activity. Furthermore, it required merely 256 mV and

357 mV vs. RHE to attain 100 and 500 mA cm^{-2} , respectively outperforming both pristine materials and several previously reported electrocatalysts (Table S2).

To gain further insights into the reaction kinetics, Tafel plots from the polarization curves and is shown in Fig. 5b. The calculated Tafel slopes for TiNb-MXene, MNS and MNS@TiNb-MXene are 97.86, 129.49 and $82.30 \text{ mV dec}^{-1}$, respectively. The significantly lower Tafel slope of the MNS@TiNb-MXene electrode indicates accelerated charge transfer kinetics and a favorable HER pathway. The slope value suggests that the reaction proceeds via the Volmer-Heyrovsky mechanism, with the Heyrovsky step (electrochemical desorption of H^*) serving as the rate-determining step, leading to H_2 evolution [65–67].

The multi-step chronopotentiometry (Fig. 5c) conducted at escalating current densities ($1\text{--}100 \text{ mA cm}^{-2}$) reveals the composite's rapid potential response and excellent adaptability to dynamic current variations. Moreover, the two-step chronopotentiometry at 10 and 100 mA cm^{-2} for 500 min (Fig. 5d) exhibits negligible potential decay, confirming the composite's long-term stability and operational under varying loads for longer durations. The outstanding durability, versatility, and ultrafast electrochemical response are attributed to the structural resilience of MXene's robust interfacial bonding and the uniform charge distribution of $\text{Mn}^{3+}/\text{Ni}^{3+}$ active sites.

Electrochemical impedance spectroscopy (EIS) was employed to evaluate the interfacial charge-transfer dynamics at the electrode-electrolyte interface near the HER potential region, within a frequency range of 1 MHz to 0.1 Hz. The Nyquist plots (Fig. 5e and Figure S6a) reveal that MNS@TiNb-MXene exhibits a significantly smaller semi-circle, corresponding to a lower charge-transfer resistance (R_{ct}) than the pristine materials, implying the formation of heterointerface-induced electron delocalization. The Bode phase angle plots (Figure S6b) show that all three samples converge to lower phase angles at higher frequencies ($\log f < 3$), reflecting predominant resistive behaviour. Notably, the MNS@TiNb-MXene composite displays a lower phase angle ($\sim 50^\circ$) compared to TiNb-MXene and MNS, suggesting reduced capacitive characteristics and enhanced electrical conductivity. The impedance-magnitude Bode plots (Figure S6c) further corroborate these findings, showing consistently lower impedance for the composite across the entire frequency spectrum. Pristine TiNb-MXene shows a relatively high charge transfer resistance and phase angle of 25° at lower frequency ($\log f = -1$), consistent with restacking and surface oxidation observed by TEM and XPS analysis. The composite effectively mitigates these limitations, showing lower R_{ct} attributed through $\text{Mn}^{3+}/\text{Ni}^{3+}$ -Se-O-MXene interfacial bonding, as evidenced by XPS, which prevents oxidation and stabilizes the electronic structure. The synergistic combination of highly conductive TiNb-MXene and abundant Mn/Ni redox-active sites minimizes charge-transfer resistance and optimizes hydrogen adsorption energy, thereby facilitating rapid electron transport, stabilized intermediate states, and efficient H^* generation for enhanced HER activity.

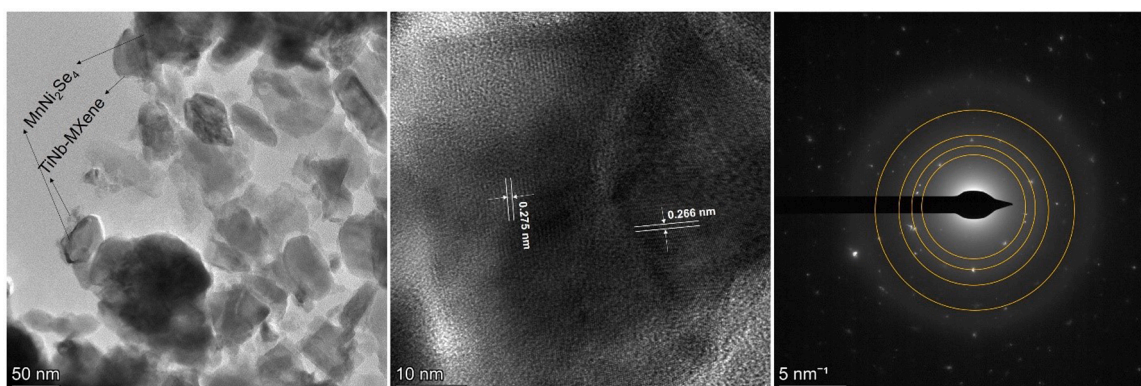


Fig. 4. a) TEM, b) HRTEM and c) SAED pattern of MNS@TiNb-MXene.

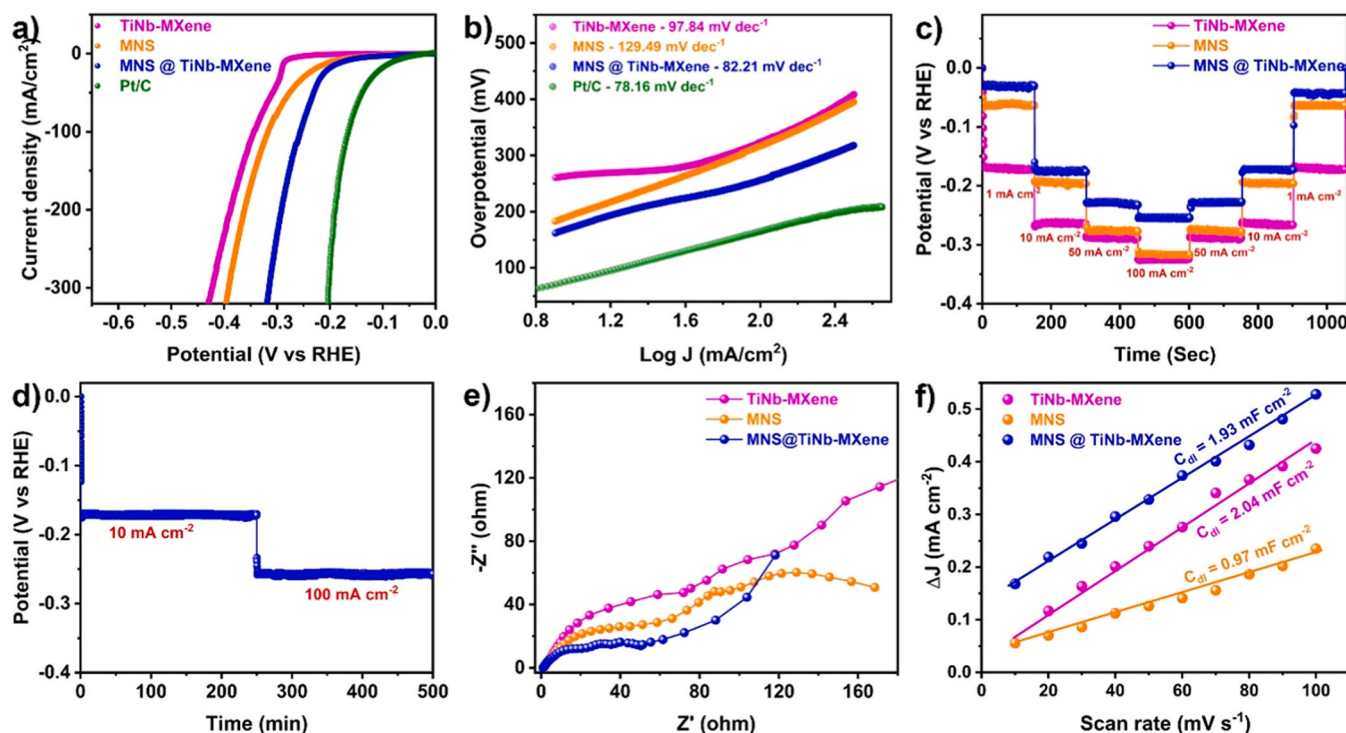


Fig. 5. HER performance of the prepared electrocatalysts in 1 M KOH, a) LSV curves at 2 mV s^{-1} , b) corresponding Tafel slopes, c) multi-step chronopotentiometry at various current densities, d) two-step chronopotentiometry, e) EIS Nyquist plots, and f) C_{dl} calculation at different scan rates.

The intrinsic electrocatalytic properties such as exchange current density (j_0), electrochemically active surface area (ECSA), turnover frequency (TOF), and mass activity, were further investigated to elucidate the HER performance of the prepared catalysts. By extrapolating the Tafel plots to zero overpotential, the MNS exhibited the highest j_0 value (0.356 mA cm^{-2}), surpassing that of TiNb-MXene (0.049 mA cm^{-2}) and the MNS@TiNb-MXene composite (0.074 mA cm^{-2}), indicating superior intrinsic electron transfer capability at lower overpotentials. However, due to synergistic interfacial coupling between MnNi_2Se_4 and TiNb-MXene, the composite demonstrates enhanced charge-transfer kinetics, higher electrical conductivity, better active sites utilization and outperforms both pristine materials at higher current densities. The ECSA values, derived from the double-layer capacitance method (Fig. 5f), were 24.13, 50.88, and 48.25 cm^2 for MNS, TiNb-MXene, and MNS@TiNb-MXene, respectively. The relatively higher ECSA of TiNb-MXene is attributed to its abundant accessible surface sites, some of which may become partially shielded upon MNS deposition in the composite. Despite this, the heterointerface promotes efficient charge redistribution and active site utilization. The TOF, calculated from the surface concentration of active sites and normalized polarization data (Figure S9a), reaches 36.1 s^{-1} at 250 mV for MNS@TiNb-MXene, outperforming TiNb-MXene (22.5 s^{-1}) and MNS (30.5 s^{-1}). Furthermore, the mass activity of the composite was evaluated based on the mass loading of the catalysts in mg cm^{-2} (Table S3). The MNS@TiNb-MXene achieves 20 A g^{-1} at 200 mV, considerably exceeding those of its pristine counterparts, confirming its high intrinsic catalytic efficiency and effective utilization of active species.

These outstanding results arise from the engineered interfacial synergy between $\text{Mn}^{3+}/\text{Ni}^{3+}$ -Se redox pairs and the highly conductive TiNb-MXene framework. The heterojunction effectively facilitates charge transport, optimizes H^+ adsorption/desorption dynamics, and accelerates the reaction kinetics for favorable H^+ intermediate stabilization. These attributes collectively ensure its superior catalytic activity, and operational robustness, and stable operation at a device-relevant high current density under demanding electrochemical conditions.

3.7. OER performance studies

Following the HER evaluation, the bifunctional performance of the catalysts was investigated via OER measurements under identical experimental conditions. Polarization curves obtained from the reverse scan were used to minimize the influence of anodic peak interference arising from Ni oxidation. As shown in Fig. 6a, the MNS@TiNb-MXene composite required overpotentials of 232 and 335 mV vs. RHE to achieve current densities of 10 and 100 mA cm^{-2} , respectively, outperforming the pristine MNS (314 and 423 mV vs. RHE) and TiNb-MXene (347 and 478 mV vs. RHE). Tafel analysis (Fig. 6b) further reveals the OER kinetics, with MNS@TiNb-MXene exhibiting a smaller slope of $105.21 \text{ mV dec}^{-1}$, indicative of more favourable catalytic kinetics compared to the individual components. The Slope value typically corresponds to a mechanism where the first electron transfer step (M-OH intermediates) is the rate-determining step, commonly observed for TMs and TMOs.

Multi-step and two-step chronoamperometry measurements under dynamic current conditions for short and extended durations (Fig. 6c, d) demonstrate the excellent durability of the MNS@TiNb-MXene composite and its rapid potential adaptability, with negligible potential decay. Charge-transfer kinetics, evaluated through Nyquist and Bode analyses (Fig. 6e and Figure S13), reveal that the composite exhibits lower R_{ct} values compared to pristine MNS and TiNb-MXene. The impedance-magnitude Bode plots show reduced impedance across the frequency spectrum, while the phase-angle Bode plots display a lower phase angle ($\sim 45^\circ$) for the composite, indicating enhanced interfacial conductivity and rapid charge-transfer capability. Collectively, these results confirm that the intrinsic conductivity of TiNb-MXene, combined with strong surface interactions among Mn, Ni, and Se species, synergistically enhances the composite's electronic properties, contributing to its superior electrocatalytic performance.

To further evaluate the intrinsic OER performance of the electrocatalyst and elucidate its mechanistic behaviour, several key metrics were analysed. The exchange current density (j_0), obtained by extrapolating the Tafel plots, indicates that the MNS@TiNb-MXene composite

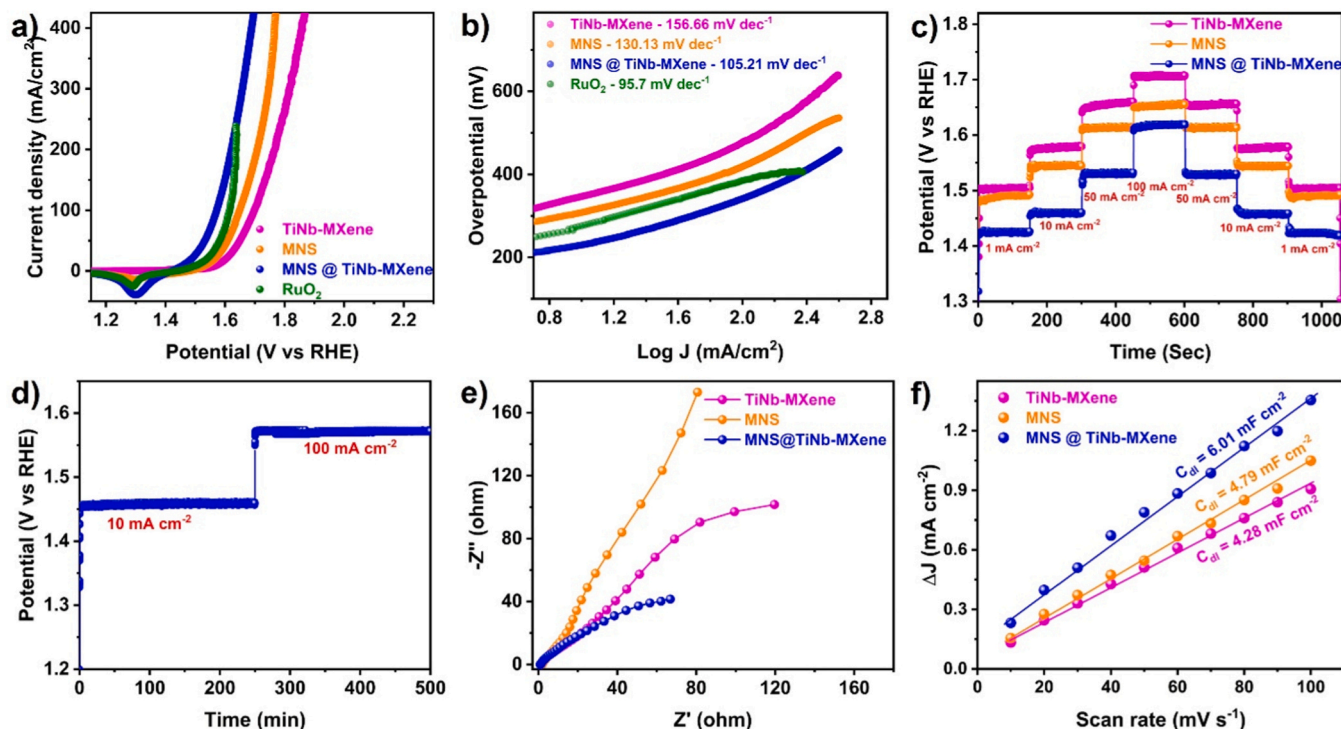


Fig. 6. OER performance of the prepared electrocatalysts in 1 M KOH, a) LSV curves at 2 mV s^{-1} , b) corresponding Tafel slopes, c) multi-step chronopotentiometry, d) two-step chronopotentiometry, e) EIS Nyquist plots, and f) C_{dl} calculation at different scan rates.

(0.258 mA cm^{-2}) is approximately 2.5- and 3-fold higher than pristine MNS and TiNb-MXene, respectively, reflecting its superior intrinsic OER

activity. The electrochemically active surface area (ECSA, Fig. 6f) of the composite (150.13 cm^2) also exceeds that of MNS (119.5 cm^2) and

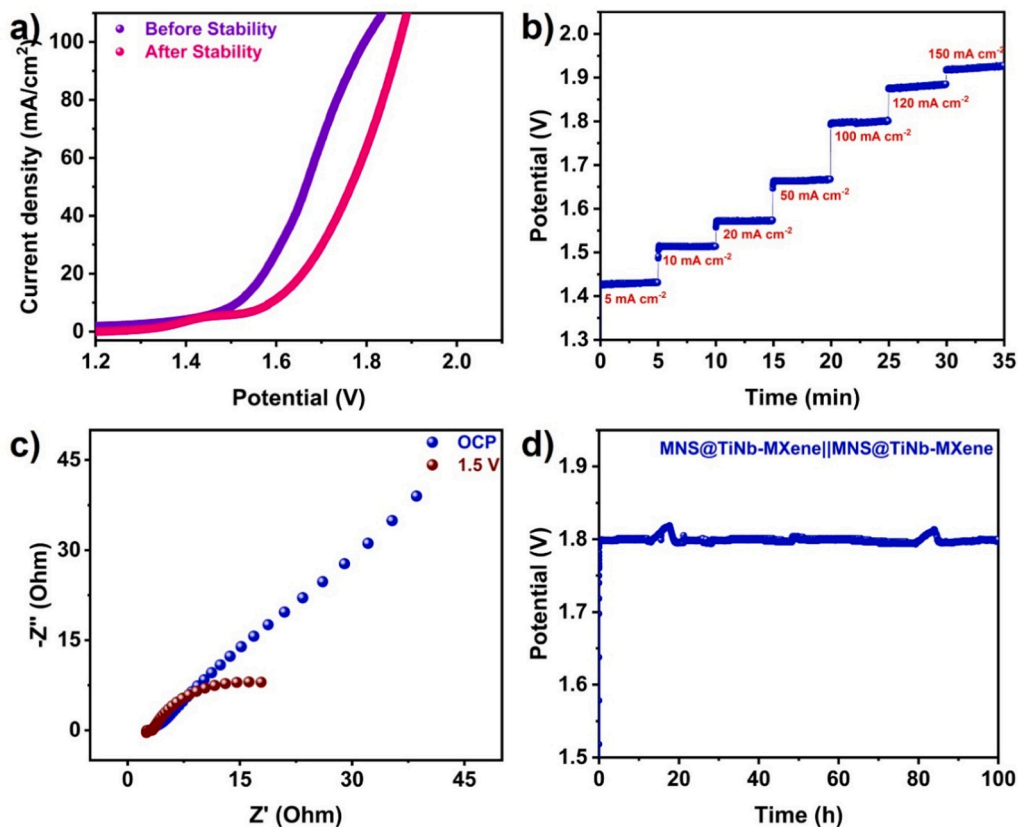


Fig. 7. Overall water splitting performance of MNS@TiNb-MXene in 1 M KOH, a) Polarization curves before and after stability test, b) Multi-step chronopotentiometry at different current densities for 5 mins, c) Nyquist plots at OCP and 1.5 V, and d) Long-term stability at 100 mA cm^{-2} for 100 h.

TiNb-MXene (107 cm^2), indicating greater surface roughness and a higher density of exposed active sites. The turnover frequency (TOF), derived from the normalized polarization curves (Figure S15a), reaches 26.25 s^{-1} at an overpotential of 350 mV for MNS@TiNb-MXene, outperforming MNS (20.9 s^{-1}) and TiNb-MXene (19.7 s^{-1}), demonstrating superior instantaneous catalytic efficiency for water oxidation. Additionally, the composite exhibits excellent mass activity, achieving 20 A g^{-1} at 280 mV, which is significantly better than that of MNS (370 mV) and TiNb-MXene (395 mV) under alkaline OER conditions (Figure S15b).

These results highlight that the $\text{Mn}^{3+}/\text{Ni}^{3+}$ redox centres facilitate the formation of OER intermediates ($\text{*OH} \rightarrow \text{*OOH}$) and stabilize the *OOH species, promoting efficient O_2 evolution. Furthermore, the incorporation of Se contributes electronic, structural, and interfacial synergistic effects, collectively enhancing OER activity [68–70]. The strong interfacial bonding between MnNi_2Se_4 and $\text{Ti}_2\text{NbC}_2\text{Tx}$ MXene, combined with optimized electrode kinetics and uniform charge distribution across the redox centres, significantly improves catalytic efficiency under alkaline OER conditions.

3.8. Overall water splitting performance studies

To evaluate the practical applicability of the MNS@TiNb-MXene composite for overall water splitting, a two-electrode cell was constructed using the material as both anode and cathode. Similar to the OER measurements, reverse-scan polarization curves were employed to minimize interference from anodic Ni oxidation peaks. As shown in Fig. 7a, the assembled cell achieved current densities of 10, 50, and 100 mA cm^{-2} at cell voltages of 1.514, 1.65, and 1.79 V, respectively, surpassing a state-of-the-art $\text{Pt/C}||\text{RuO}_2$ full cell, which required 1.56 and 1.75 V to reach 10 and 100 mA cm^{-2} . These results also outperform most reported electrocatalysts (Table S4). Multi-step chronoamperometry (Fig. 7b) confirms the composite's rapid response to dynamic current loads, demonstrating its potential for practical applications under real-time, fluctuating power supply conditions. Electrochemical impedance spectroscopy (EIS) was conducted at different applied potentials (1.0 and 1.5 V) to probe charge-transfer kinetics during water electrolysis. The Nyquist plot (Fig. 7c) indicates that the full cell exhibits a charge-transfer resistance (R_{ct}) of 7.8Ω at open-circuit potential (OCP), which decreases to 3.4Ω at 1.5 V. Corresponding Bode plots (Figure S16) show a lower phase angle ($\sim 35^\circ$) and reduced impedance ($\log |Z| \approx 1.29 \Omega$) at 1.5 V compared to OCP ($\sim 45^\circ$, $\log |Z| \approx 1.75 \Omega$), reflecting enhanced interfacial charge transfer, reduced capacitive behavior, and improved kinetics for overall water splitting.

The long-term operational stability of the MNS@TiNb-MXene electrolyzer under alkaline conditions was evaluated via chronopotentiometry at a higher current density of 0.1 A cm^{-2} for 100 h (Fig. 7d). Minor potential fluctuations observed at 17, 49, and 84 h are attributed to the temporary obstruction of active sites by gas bubbles. Upon bubble detachment, the active sites are restored, and the potential returns to its initial value, demonstrating the composite's resilience and stability over extended operation [71,72]. After 100 h, a slight increase in overpotential from 1.79 to 1.85 V at 100 mA cm^{-2} was observed in the polarization curve corresponding to the potential drift of $\sim 0.6 \text{ mV h}^{-1}$, confirming the exceptional durability and robustness of the MNS@TiNb-MXene bifunctional electrocatalyst under sustained high current density alkaline electrolysis conditions. The slight increase in overpotential after 100 h may be attributed to gradual surface oxidation, minor active site reconstruction, or mechanical detachment of a small fraction due to gas bubble evolution. Despite these minor changes, the composite maintains $\sim 97\%$ of its initial activity after 100%, highlighting its robustness.

The exceptional cyclic stability of the prepared MNS@TiNb-MXene hybrid electrocatalyst can be attributed to the strong interfacial interaction between MnNi_2Se_4 nanoparticles with the conductive TiNb-MXene nanosheets. The synergistic stabilization at the heterointerface

by coupling the MXene framework with covalent Se-O-MXene bonding is evidenced by XPS. While the conductive MXene framework provides structural support and an efficient electron transfer pathway, the uniformly distributed MnNi_2Se_4 with covalent bonding suppresses the nanoparticle agglomeration and mitigates MXene restacking. The charge redistribution, robust MXene structural integrity and MXene-mixed metal selenides heterostructure are a collective multi-level stabilization strategy that helps to maintain the material's integrity, thereby preserving accessible active sites and ensuring stable electrochemical performances.

3.9. Supercapacitor performance studies

3.9.1. Three-electrode cell studies

Following the evaluation of its bifunctional catalytic activity, the MNS@TiNb-MXene composite was further investigated as a supercapacitor electrode. The charge-storage behaviour was analysed using a three-electrode configuration, with a Pt wire as the counter electrode, Ag/AgCl as the reference electrode, and the prepared materials supported on nickel foam as the working electrode. As shown in Fig 8a, the cyclic voltammetry (CV) curves at 5 mV s^{-1} reveal the hybrid capacitive nature of the materials, with distinct redox peaks indicating a combination of electric double-layer capacitance (EDLC) and faradaic processes. These arise from the reversible oxidation/reduction of Ti/Nb and Mn/Ni species, along with the adsorption/desorption of K^+ ions at the active sites. Notably, the MNS@TiNb-MXene composite exhibits a larger integrated CV area compared to the pristine materials, reflecting the synergistic effect between the Mn/Ni-Se redox activity and the intrinsic conductivity of MXene.

The CV curves of MNS and MNS@TiNb-MXene recorded at different scan rates from 5 to 100 mV s^{-1} (Fig. 8b,c) exhibit pronounced redox peaks between 0.1 and 0.5 V vs. Ag/AgCl, confirming reversible faradaic charge storage via Mn/Ni redox transitions in MNS. The superior performance of the composite is attributed to the combined contributions of Mn/Ni and Ti/Nb redox processes. With increasing scan rates, the cathodic and anodic peaks shift toward more negative and positive potentials, respectively, due to ohmic polarization and kinetic limitations in ion diffusion within the electroactive material. The linear increase in peak current and the retention of peak shapes with scan rate indicate a surface-controlled pseudocapacitive behaviour and excellent electrochemical reversibility [73,74]. The enhanced performance of MNS@TiNb-MXene arises from the synergistic architecture of MXene's conductive matrix and the covalent Se-O-MXene bonds, which stabilize Mn/Ni redox sites and facilitate efficient charge storage.

The charge-storage mechanism of the prepared electrode materials was further analysed via galvanostatic charge-discharge (GCD) measurements. The GCD profiles at 1 A g^{-1} (Fig. 8d) show a characteristic discharge plateau with an extended discharge time for the MNS@TiNb-MXene composite (1634 s), outperforming the pristine TiNb-MXene and MNS electrodes. The observed non-linear charge-discharge curves with subtle voltage plateaus and minimal iR drop indicate a hybrid charge-storage behaviour [75,76]. The enhanced performance of the composite arises from its synergistic architecture, which provides an effective conductive network, improved ion accessibility, and mitigates MXene restacking, thereby increasing the overall capacitance. The specific capacitances calculated at 4 A g^{-1} are 440, 954.8, and 1648.24 F g^{-1} for TiNb-MXene, MNS, and MNS@TiNb-MXene, respectively. Fig. 8e,f shows the GCD curves of MNS and MNS@TiNb-MXene over current densities ranging from 1 to 20 A g^{-1} . The quasi-triangular, non-linear profiles with potential plateaus corroborate the faradaic charge-storage mechanism, consistent with the CV analysis. The specific capacitance of each electrode as a function of current density is summarized in Figure S16.

Electrochemical impedance spectroscopy (EIS) measurements at open-circuit potential (OCP) reveal that the MNS@TiNb-MXene composite exhibits a significantly lower charge-transfer resistance ($R_{ct} \approx 60$

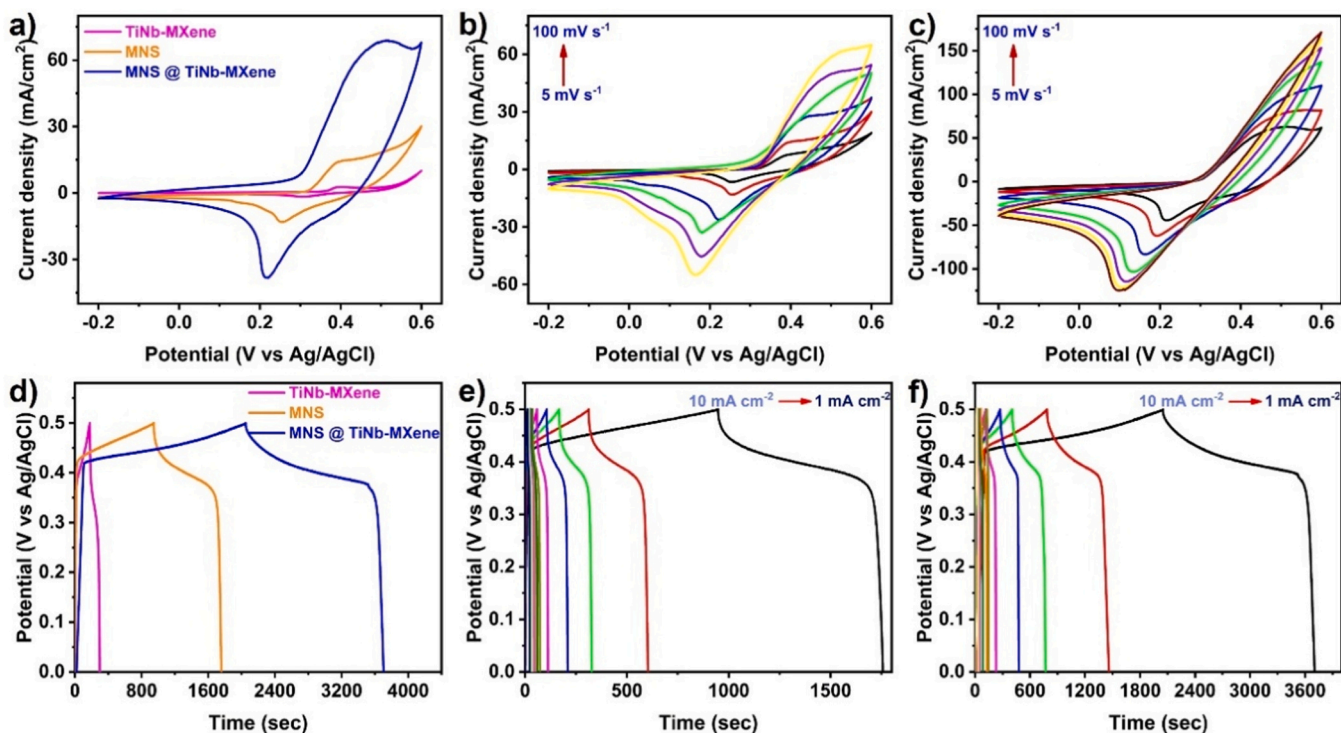


Fig. 8. Three-electrode supercapacitor performance, a) CV curves of TiNb-MXene, MNS and MNS@TiNb-MXene at 5 mV s^{-1} , b) & c) CV curves of MNS and MNS@TiNb-MXene from 5 to 100 mV s^{-1} , d) GCD plots of TiNb-MXene, MNS and MNS@TiNb-MXene at 2 mA cm^{-2} , and e) & f) GCD plots of MNS and MNS@TiNb-MXene at current densities ranging from 1 to 10 mA cm^{-2} .

Ω) compared to the pristine TiNb-MXene and MNS electrodes. Analysis of the phase-angle and impedance magnitude-dependent Bode plots further supports these findings, with the composite showing a lower

phase angle ($\sim 50^\circ$) and reduced impedance across the frequency spectrum, indicative of superior capacitive behaviour and faster ion transport dynamics. The shift of the peak phase angle toward lower

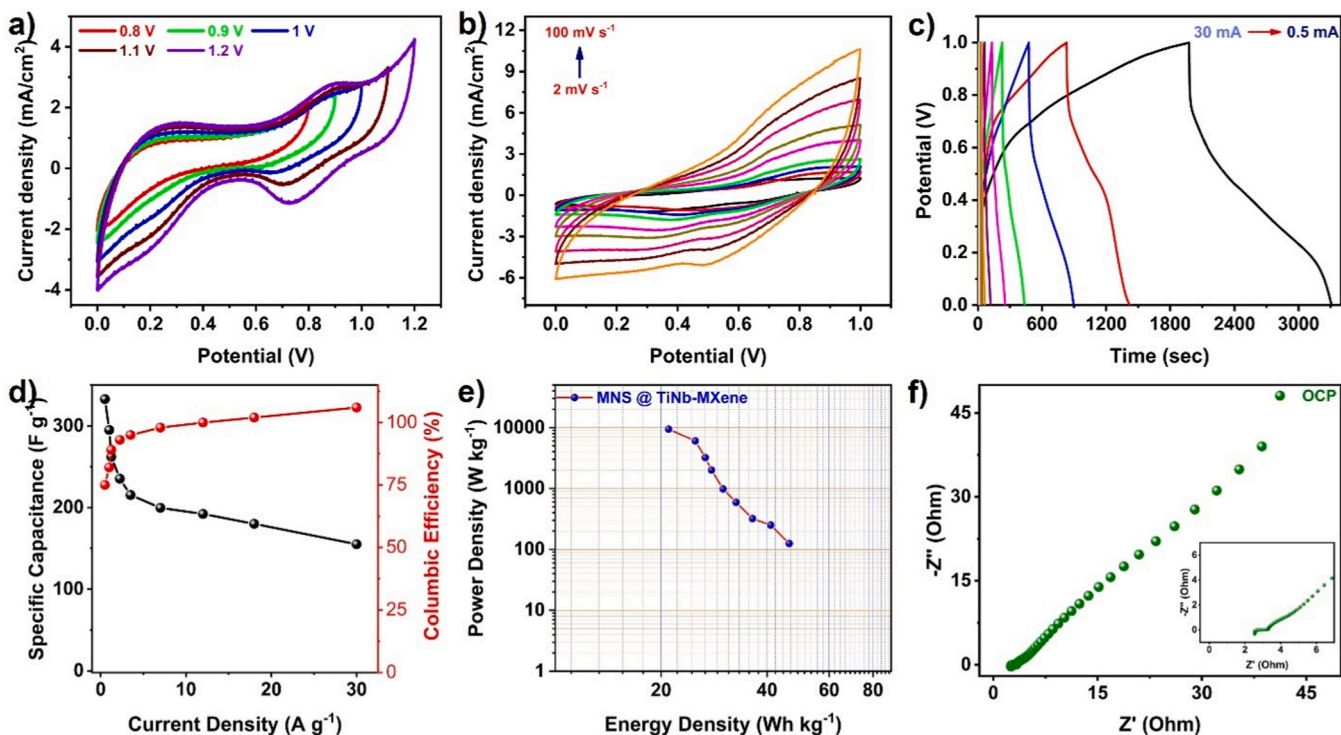


Fig. 9. Two-electrode symmetric supercapacitor performance of MNS@TiNb-MXene, a) CV curves at 10 mV s^{-1} over different potential windows, b) CV curves at scan rates from 2 to 100 mV s^{-1} , c) GCD profiles at current densities from 0.5 to 30 mA cm^{-2} , d) Specific capacitance and columbic efficiency as a function of current density, e) Ragone's plot, and f) EIS Nyquist plot at OCP.

frequencies suggests prolonged relaxation times and efficient diffusion-controlled charge storage. These results demonstrate that the enhanced electrochemical performance arises from synergistic interfacial interactions rather than simple additive effects. The exceptional capacitance, improved charge-storage capability, and rate performance of MNS@TiNb-MXene are attributed to the strong interfacial coupling between MXene and MnNi₂Se₄. Furthermore, the presence of Mn/Ni vacancies introduces additional electrochemically active sites, promoting enhanced ion diffusion and facilitating effective electrolyte penetration. The 2D conductive network of MXene not only improves electron mobility and optimizes charge-transfer pathways but also provides additional active sites for Mn/Ni redox reactions, contributing extra pseudocapacitive behaviour to the composite.

3.9.2. Two-electrode cell studies

To evaluate the practical applicability of MNS@TiNb-MXene, a symmetric supercapacitor cell (SSC) was fabricated using the composite, with each electrode having a mass loading of approximately 1.2 mg cm⁻² in 1 M KOH. The optimal potential window was determined from CV measurements at 10 mV s⁻¹ over different ranges (Fig. 9a). The CV curves exhibit a quasi-rectangular shape with negligible redox peaks, indicating ideal capacitive behaviour and excellent electrochemical stability within the working potential window. CV curves recorded at scan rates from 2 to 100 mV s⁻¹ (Fig. 9b) maintain their shape, demonstrating high reversibility and low internal resistance. The GCD profiles (Fig. 9c) show nearly symmetric charge-discharge behaviour across all tested current densities, confirming the excellent supercapacitive performance and high Coulombic efficiency of the SSC. From the GCD curves, the specific capacitance of the cell is calculated to be 295 F g⁻¹ (295 C g⁻¹, 98.33 mAh g⁻¹) at 1 A g⁻¹, surpassing many previously reported symmetric supercapacitors. The variation of specific capacitance and Coulombic efficiency with current density is presented in Fig. 9d, showing sustained high efficiency even at elevated current densities.

Electrochemical impedance spectroscopy (EIS) was performed at open-circuit potential (OCP) to investigate the charge-transfer and ion-transport behaviour of the symmetric supercapacitor. The Nyquist plot (Fig. 9f) shows low solution resistance ($R_s \approx 7.12 \Omega$) and charge-transfer resistance ($R_{ct} \approx 8.4 \Omega$), indicating excellent conductivity. Analysis of the Bode plots (Figure S19b) reveals higher phase angles and impedance magnitudes at lower frequencies, supporting a capacitive and diffusion-controlled charge-storage process. The non-monotonic decrease in phase angle suggests the coexistence of multiple electrochemical processes, while the dominant intrinsic resistance at higher frequencies results in lower phase angles and impedance magnitudes. The outstanding performance of the SSC arises from the strong interfacial synergy between the MXene framework and MnNi₂Se₄ nanoparticles. This architecture combines the metallic conductivity and structural robustness of MXene with the redox activity of Se and Mn/Ni ions, providing an abundance of electroactive sites, efficient charge-transfer pathways, and excellent structural stability.

The designed synthesis strategy for MNS@TiNb-MXene endows the composite with remarkable structural and electrochemical advantages. The formation of bimetallic selenides results in mixed oxidation states of Mn and Ni, providing a higher density of active sites, optimized adsorption energies, and enhanced catalytic performance [77,78]. Selenium, simultaneously binding with TiNb-MXene and Mn/Ni, improves electronic conductivity by facilitating efficient electron transport and occasionally acting as an active site for catalytic reactions. Beyond electrocatalysis, these features significantly enhance the electrochemical behaviour for supercapacitor applications. Mn and Ni cations contribute to pseudocapacitance through faradaic redox reactions, while TiNb-MXene provides electric double-layer capacitance and high conductivity. The strong interfacial interactions, coupled with the unique hierarchical morphology and uniform distribution of Mn-Ni-Se within the composite, promote rapid charge transfer, improve electron and ion

mobility, increase accessibility of active sites, and boost catalytic activity. This synergistic architecture underpins the superior electrocatalytic performance, durability, structural integrity, and overall stability of MNS@TiNb-MXene under harsh alkaline conditions, while simultaneously enhancing capacitance, energy density, and cycling stability in supercapacitor applications.

4. Conclusions

In summary, the MnNi₂Se₄-decorated Ti₂NbC₂T_x MXene hybrid (MNS@TiNb-MXene) was successfully engineered via a two-step solvothermal process, embedding the nanoparticles within the conductive MXene scaffold. The composite exhibits outstanding bifunctional performance, achieving low overpotentials of 173 mV for HER and 230 mV for OER, with the full electrolyzer cell of just 1.514 V to reach 10 mA cm⁻². EIS analyses (Nyquist and Bode plots) indicate low resistance and rapid charge transfer, driven by strong interfacial interactions, which is corroborated by XPS results showing Se-O-MXene bond formation in the Se 3d spectra. For supercapacitor applications, MNS@TiNb-MXene demonstrates strong energy storage capability, delivering a high specific capacitance of 2106 F g⁻¹ at 1 A g⁻¹ in a three-electrode setup, and the assembled symmetric cell achieves 313.5 F g⁻¹ at 1 A g⁻¹, along with an energy density of 43.4 Wh kg⁻¹ at a power density of 0.75 kW kg⁻¹. While the present study provides strong experimental evidence for interfacial coupling based on Raman, XPS, and HRTEM analyses, further investigation using atomic-resolution STEM techniques (e.g., HAADF-STEM) and DFT calculations would offer deeper insight into the atomic/electronic structure, charge-transfer mechanisms, and adsorption energetics at the heterostructure interface. These studies are planned as part of future work. By leveraging synergistic interfacial engineering, this study demonstrates a viable strategy for developing MXene-based hybrid as a dual-functional electrode capable of high-efficiency electrocatalysis and energy storage, representing a significant advancement toward sustainable, industrial-scale energy conversion and storage technologies.

CRedit authorship contribution statement

S P Arunachalakumar: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sen-thilkumar Ramasamy:** Writing – review & editing, Formal analysis. **Narendhar Chandrasekar:** Writing – review & editing, Formal analysis. **Saradh Prasad Rajendra:** Writing – review & editing, Formal analysis. **Khalid Eidah Alzhrani:** Writing – review & editing, Formal analysis. **Seung Jun Lee:** Writing – review & editing, Funding acquisition. **Subramania Angaiah:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Conceptualization.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jallcom.2026.188460](https://doi.org/10.1016/j.jallcom.2026.188460).

Data Availability

Data will be made available on request.

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