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Mn-doped CoSe₂ nanosheets as high-efficiency catalysts for the oxygen evolution reaction†

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In this work, we introduce for the first time an aqueous solution method followed by a selenization step to prepare Mn-doped CoSe₂ nanosheets supported on nickel foam for the oxygen evolution reaction. These findings provide us highly efficient electrocatalysts instead of noble metal catalysts for the oxygen evolution reaction.

Electrochemical water splitting offers us a promising method for the conversion of renewable resources to clean hydrogen energy.^{1,2} The sluggish kinetics of the oxygen evolution reaction (OER) generating a high overpotential have limited the practical applications of electrocatalytic water splitting.^{3,4} Precious metal oxides, such as IrO₂ and RuO₂, can effectively lower the overpotential of the OER, but their large scale applications are difficult to realize due to scarcity and exorbitant price.^{5,6} Hence, there is an urgent need to design and exploit efficient and stable non-noble metal catalysts that can promote the efficiency of water splitting.⁷ Of note, cobalt-based compounds have been demonstrated to be robust electrocatalysts for the OER in alkaline electrolytes, sparked by their mixed rich valence states, intrinsic conductivity, high corrosion stability and earth-abundance.^{8,9} In particular, CoSe₂, with a cubic structure and t_{2g}⁶e_g¹ electronic configuration, has garnered considerable attention.^{10,11} For instance, Park *et al.* reported CoSe₂ nanocrystal OER catalysts with an overpotential of 430 mV to achieve a current density of 10 mA cm⁻².¹² Yu *et al.* prepared mesostructured CoSe₂/diethylenetriamine (DETA) nanobelts, delivering a current density of 10 mA cm⁻² upon the application of 468 mV overpotential.¹³ Nevertheless, the OER performance of most CoSe₂ catalysts still cannot surpass

the commercial IrO₂ and RuO₂ catalysts. To this end, significant advances in improving the catalytic performance of CoSe₂ have been made. A second metal doping process has proved to be useful to engineer the surface electronic density and active sites, thus offering great benefits to favor the enhancement of catalytic activity.¹⁴⁻¹⁶ Motivated by the above mentioned, we have synthesized Mn-doped CoSe₂ nanosheets supported on nickel foam (Mn-CoSe₂/NF) using the Co-based metal organic framework (Co-MOF) as the precursor. Mn was chosen as the doping element due to the fact that the formation of the Mn-Co bond can contribute to enhance the OER kinetics and accelerate the oxygen evolution rate efficiently. When applied as catalysts, the as-prepared Mn-CoSe₂/NF nanosheets demand only a low overpotential of 296 mV to reach a current density of 100 mA cm⁻² and show outstanding stability in 1 M KOH.

The structural morphologies of the as-synthesized samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1a clearly shows numerous nanosheets evenly covering the Ni foam substrate.

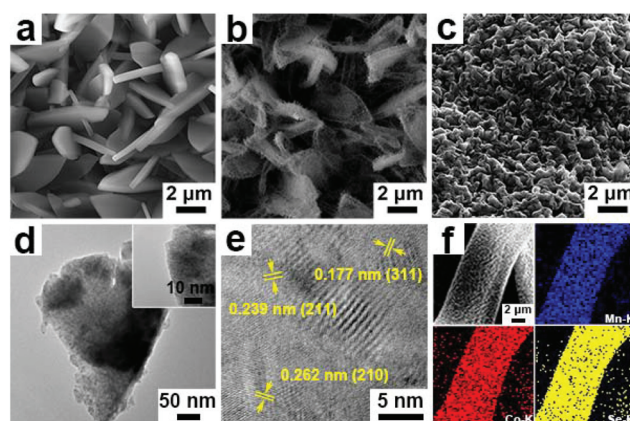


Fig. 1 SEM images of (a) Co-MOF, (b) MnCo LDH and (c) Mn-CoSe₂/NF nanosheets. (d) TEM, (e) HRTEM and (f) EDX elemental mapping images of Mn-CoSe₂/NF nanosheets.

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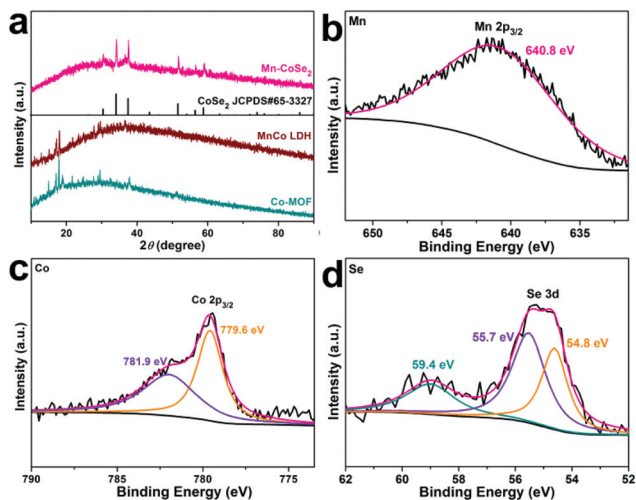


Fig. 2 (a) XRD patterns of Co-MOF, MnCo LDH and Mn-CoSe₂/NF nanosheets. High resolution XPS spectra of (b) Mn 2p_{3/2}, (c) Co 2p_{3/2} and (d) Se 3d for Mn-CoSe₂/NF nanosheets.

Moreover, the corresponding XRD pattern matches well with that of Co-MOF (Fig. 2a and S1†). After being etched with Mn(NO₃)₂, the Co-MOF/NF precursors are successfully converted into MnCo LDH/NF (Fig. 2a). Obviously, the etched product still maintains the sheet-like morphology but with a rougher surface (Fig. 1b). The subsequent selenylation ensures the formation of Mn-CoSe₂/NF with a similar nanosheet structure (Fig. 1c and d). In Fig. 1e, the HRTEM image displays well-resolved lattice fringes of 0.262, 0.239 and 0.177 nm, corresponding to the (210), (211) and (311) planes of CoSe₂, respectively.¹⁷ The energy-dispersive X-ray (EDX) mapping analysis in Fig. 1f further illustrates the uniform distribution of the Mn, Co and Se elements. Besides this, the ratio of Mn : Co : Se is estimated to be close to 0.22 : 1 : 2.06 by inductively coupled plasma-mass spectrometry (ICP-MS), further confirming the successful synthesis of Mn-doped CoSe₂/NF nanosheets.

Fig. 2a shows the X-ray diffraction (XRD) patterns of Co-MOF, MnCo LDH and Mn-CoSe₂/NF nanosheets. Except for the peaks at 44.5 and 51.8° from the substrate (JCPDS No. 65-2865), the additional diffraction peaks show a strong similarity to those of CoSe₂ (JCPDS No. 65-3327),¹⁸ but a slight shift toward lower angles owing to the doping of Mn. Additionally, no typical signals of the MnSe₂ phase have been identified, in accordance with the HRTEM results. We further study the chemical valence state of Mn-CoSe₂ nanosheets by X-ray photoelectron spectroscopy (XPS). In Fig. 2b, the Mn 2p_{3/2} spectrum exhibits a broad peak at 640.8 eV, which can be indexed to Mn²⁺.¹⁹ As for the Co 2p_{3/2} spectrum (Fig. 2c), the binding energies at 779.6 and 781.9 eV suggest the coexistence of Co³⁺ and Co²⁺ in CoSe₂.^{20,21} In the Se 3d region (Fig. 2d), the peaks located at 54.8 and 55.7 eV are assigned to Se 3d_{5/2} and Se 3d_{3/2} of the Se-Co bonds in CoSe₂,^{22,23} while the peak positioned at 59.4 eV reveals the presence of Se oxide species.²⁴

The OER activities of Mn-CoSe₂/NF catalysts were evaluated in 1 M KOH with a typical three-electrode setup at room temp-

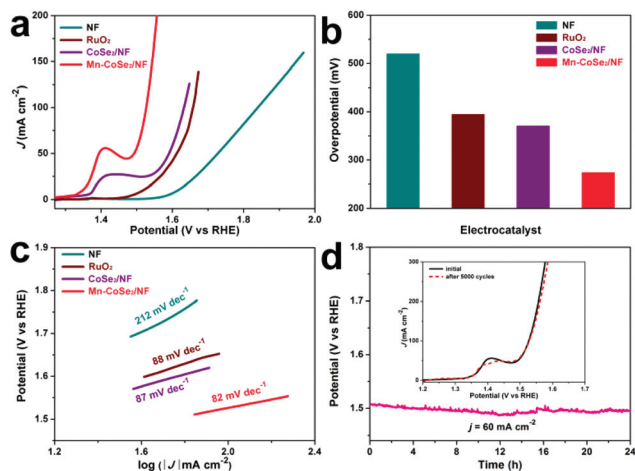


Fig. 3 OER performance of NF, commercial RuO₂, CoSe₂/NF and Mn-CoSe₂/NF catalysts in 1 M KOH: (a) iR-corrected polarization curves, (b) Overpotentials at a current density of 60 mA cm⁻², (c) Corresponding Tafel plots, (d) Time-dependent potential curve at a constant current density of 60 mA cm⁻² for 24 h (inset: a comparison of polarization curves before and after 5000 CV cycles).

erature. We applied iR compensated to all the polarization curves unless otherwise stated. Fig. 3a compares the polarization curves measured at a scan rate of 1 mV s⁻¹ of different catalysts. Evidently, the Mn-CoSe₂/NF catalysts exhibit lower overpotentials of 274 and 296 mV for 60 and 100 mA cm⁻² compared to those of NF (521 mV at 60 mA cm⁻², 610 mV at 100 mA cm⁻²), commercial RuO₂ (395 mV at 60 mA cm⁻², 428 mV at 100 mA cm⁻²) and CoSe₂/NF (371 mV at 60 mA cm⁻², 402 mV at 100 mA cm⁻²), implying remarkable electrocatalytic activities for the OER (Fig. 3b). Our Mn-CoSe₂/NF catalysts also compare favorably to most Co-based catalysts reported previously (see Table S1†). Furthermore, the corresponding Tafel slopes of NF, RuO₂, CoSe₂/NF and Mn-CoSe₂/NF catalysts are 212, 88, 87 and 82 mV dec⁻¹ (Fig. 3c), indicative of favorable reaction kinetics of Mn-CoSe₂/NF.²⁵ This is further confirmed by electrochemical impedance spectra (EIS), in which the Mn-CoSe₂/NF catalysts possess a lower charge transfer resistance, and thus a faster electron transport (Fig. S2†).^{26,27} In order to estimate the electrochemically active surface areas (ECSAs), a simple cyclic voltammetry (CV) in the non-faradaic region was performed to determine the double-layer capacitance (*C*_{dl}). As shown in Fig. S3,† the *C*_{dl} of the Mn-CoSe₂/NF catalysts (162.1 mF cm⁻²) presents about 2.5 times as high as that of the CoSe₂/NF (64.8 mF cm⁻²), revealing that more active sites are created after the introduction of Mn.^{28,29} In addition, long-term stability is another significant parameter that needs to be considered for all catalysts. For the Mn-CoSe₂/NF catalysts, the nearly constant potential for 60 mA cm⁻² under a 24 h continuous operation test and similar *i*-*v* curves before and after 5000 cycles are retained and observed (Fig. 3d), thus manifesting strong stability. Note that the surface of the Mn-CoSe₂/NF catalysts has been oxidized (Fig. S4†) and the surface generated CoSe_x really functions as

the active species.³⁰ Besides this, SEM and XRD characterizations further confirm that there is no obvious change in the morphology and structure after stability measurement (Fig. S5 and S6†). Fig. S7† reveals the O₂ production amount detected by a water-gas displacing method that matches well with the theoretically calculated value, suggesting almost 100% faradaic efficiency. The superior catalytic activities of the Mn–CoSe₂/NF catalysts could be attributed to the following factors: (1) the Jahn–Teller distortion mismatch between M–Se (M = Co and Mn) coordination octahedra induces a subtle distortion in the atomic arrangement, giving the feature of high conductivity and more active edge sites;^{31,32} (2) Mn incorporation tunes the electronic structure of CoSe₂, thereby optimizing the binding energies of the OER intermediates to promote the oxygen evolution.^{33,34}

Conclusions

In summary, Mn-doped CoSe₂ nanosheets anchored on Ni foam have been prepared by etching and selenizing a porous Co–MOF precursor. As expected, the synergistic effect of Mn and Co renders the Mn-doped CoSe₂ catalysts with a superior OER performance, with an overpotential of 296 mV at a current density of 100 mA cm⁻² and good cycling durability. Our work establishes the Mn–CoSe₂/NF nanosheets as promising OER catalysts and also provides a novel strategy to improve water oxidation by heteroatom doping.

Conflicts of interest

There are no conflicts to declare.

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