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1. Introduction

Regarding the rapid consumption of fossil fuels and increasing environmental pollution problems, it is highly expected to exploit clean and sustainable energy sources.1,2 Electrochemical water splitting is an essential and convenient technology for the production of sustainable energy sources due to its environmental benignity and high efficiency, which includes supplying molecular hydrogen via the cathodic HER and generating oxygen molecules through the anodic OER.3-5 Regardless of these advantages, the large overpotential for OER and HER severely restricted the practical application of electrochemical water splitting. Accordingly, searching for highly efficient electrocatalysts is necessary. Currently, state-of-the-art electrocatalysts for the HER and OER are Pt-group materials and Ru/Irbased oxides, respectively.6,7 However, drawbacks such as exorbitant price, limited natural reserves, and unsatisfactory performances greatly impede their practical applications. In this regard, the design and development of cost-effective and

Constructing bundle-like Co-Mn oxides and Co-Mn selenides for efficient overall water splitting[†]

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Making easy-to-make, cost-efficient, and durable electrocatalysts for overall water splitting to produce oxygen and hydrogen is of paramount significance for future renewable energy systems but is still a challenge. Herein, mesoporous CoMn and CoMnSe nanobundles are successfully constructed *via* a facile one-pot hydrothermal approach. It is discovered that the Mn introduction in Co oxides can simultaneously tune their electronic structure and modulate the nanobundle morphology. As a result, benefitting from the 3D open nanobundle structure, the self-supported Co₁Mn₁ oxide exhibits unprecedented oxygen evolution reaction (OER) activity with an ultralow overpotential of 221 mV at 10 mA cm⁻². Moreover, such a nanobundle-like structure also enables the Co₁Mn₁Se catalyst to exhibit outstanding hydrogen evolution reaction (HER) activity with a relatively low overpotential of 87.3 mV at 10 mA cm⁻², surpassing those of previously reported non-precious metal catalysts. More importantly, taking advantage of their excellent OER and HER activity, an advanced water electrolyzer through exploiting Co₁Mn₁ oxide and Co₁Mn₂Se nanobundles as the anode and cathode is fabricated, which gives an impressive water-splitting current density of 10 mA cm⁻² in 1.0 M KOH solution at 1.60 V with remarkable stability over 36 h, holding great potential for efficient overall water splitting electrocatalysis.

earth-abundant electrocatalysts for electrochemical water splitting are highly imperative.⁸⁻¹⁰

Thanks to their earth-abundant nature and theoretically excellent electrocatalytic performance, 3d transition-metal (3d TM) (e.g., Fe, Co, Ni, and Mn)-based electrocatalysts have attracted extensive attention and been generally considered as ideal substitutes for noble-metal based materials for the HER and OER,^{11,12} such as metal chalcogenides, metal alloys, and metal phosphates for the HER, metal hydroxides and metal oxides for the OER.13-22 However, 3d TMs in traditional forms such as aggregated particles or bulk counterparts generally display no competitive advantages in electrocatalysis, particularly for overall water splitting, due to their limited active surface areas and few catalytically active sites.23,24 Moreover, the catalytic activities of bare 3d TMs in high-concentration alkaline solutions and high overpotential are also unstable; all of these shortcomings have also limited their practical application to some extent. To overcome these disadvantages and obtain highactivity and stable electrocatalysts, various strategies have been well developed. And one of the most efficient approaches is to rationally design the morphology of 3d TMs since the structures of materials deeply affect their electrocatalytic properties. For the sake of increasing the utilization efficiency of catalytically active sites, precisely controlling the morphology and structure of electrocatalysts is of paramount importance for promoting electrocatalytic overall water splitting performance to a higher level.25-27 Another choice to greatly improve electrocatalytic

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performances is to form bimetal or bimetallic oxides, which can modulate their adsorption energies and electronic structures.²⁸⁻³² Besides, doping phosphorus, sulfur, or selenium into bimetallic oxides has also been generally considered as an efficient avenue for the construction of high-performance electrocatalysts for overall water splitting.³³⁻³⁷ To this end, the design and development of both efficient and stable electrocatalysts for overall water splitting by integrating the above strategies are highly desirable, but are still a grand challenge.

Motivated by the above considerations, we herein established a facile one-pot hydrothermal method for the successful construction of a novel class of nanobundle-like CoMn oxide and CoMn selenide (denoted as CoMn NBs and CoMnSe NBs) electrocatalysts, which can act as anodic and cathodic electrocatalysts for the OER and HER, respectively. Owing to the large surface area, accelerated electron mobility and mass transfer, invulnerable dissolution, and the strong synergistic coupling between Co and Mn, the resultant Co₁Mn₁ NBs can display superior OER activity with the overpotentials of only 221 and 330 mV to reach the current density of 10 and 100 mA cm^{-2} in 1.0 M KOH solution. Notably, the electrocatalysts doped with Se were fabricated for the HER, of which the optimized Co₁Mn₁Se NBs could also exhibit excellent electrocatalytic activity with an ultralow overpotential of 87.3 mV to achieve the HER current density of 10 mA cm⁻², which was much superior to that of most of the other electrocatalysts. More significantly, the optimized Co1Mn1 NBs//Co1Mn1Se NB couple could also exhibit high activity for overall water splitting with a cell voltage of only 1.60 V to afford the current density of 10 mA cm^{-2} in 1.0 M KOH solution, which was much superior to that of the Ir/C//Pt/C couple, demonstrating the potential of novel CoMn NB catalysts for application in practical water electrolysis.

2. Experimental section

2.1 Chemicals and materials

Potassium hydroxide (KOH, analytical reagent), cobaltous nitrate $(Co(NO_3)_2 \cdot 6H_2O)$, analytical reagent), manganese nitrate $(Mn(NO_3)_2 \cdot 4H_2O)$, analytical reagent), and ethylene glycol $(CH_2OH)_2$ were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Se powder and urea $(CO(NH_2)_2, 99\%)$ were purchased from Sigma-Aldrich. All the chemicals were used as received without further purification. Water (18 M Ω cm⁻¹) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

2.2 Synthesis of CoMnSe and CoMn NBs

The mesoporous CoMn NBs are synthesized by a facile one-pot hydrothermal method. In a standard synthesis, 29.1 mg $Co(NO_3)_2 \cdot 6H_2O$, 25.1 mg $Mn(NO_3)_2 \cdot 4H_2O$, 7.9 mg Se powder, and 60 mg urea were added to a solution containing 9 mL ethylene glycol and 1 mL deionized water under ultrasound irradiation for 30 min. The mixture was then transferred into a reactor and heated at 180 °C for 10 h. The products were then collected *via* centrifugation and washed several times with ethanol and acetone. The CoMn NBs were synthesized through the same approach just without the addition of 7.9 mg Se powder. And the Co(OH)₂ nanobelts (NBs) and Mn₂O₃ were also prepared under the same conditions without the addition of Se powder, Mn(NO₃)₂·4H₂O, and Co(NO₃)₂·6H₂O, respectively. For comparison, the Co₁Mn_{0.8} NBs, Co₁Mn_{1.2} NBs, Co₁Mn_{0.8}Se NBs, and Co₁Mn_{1.2}Se NBs were also synthesized under the same conditions while tuning the amount of Mn with the designed concentrations.

2.3 Characterization

Scanning electron microscopy (SEM) and energy dispersive Xray (EDX) were carried out on an XL30 ESEM FEG scanning electron microscope at a voltage of 20 kV. The transmission electron microscopy (TEM) images were acquired using a HITACHI HT7700 TEM at an accelerating voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) images, selected area electron diffraction (SAED) patterns, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained by using an FEI Tecnai F20 transmission electron microscope. Powder X-ray diffraction (PXRD) patterns were collected on an X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K α Xray source ($\lambda = 1.540598$ Å). X-ray photoelectron spectroscopy spectra (XPS) were recorded on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectroometer.

2.4 Electrochemical measurements

The electrochemical measurements were conducted with a CHI 760e electrochemical workstation, employing CoMn NBs and CoMnSe NBs as working electrodes, a Ag/AgCl electrode as the reference electrode, and a carbon rod as the counter electrode, respectively. To prepare the working electrodes, 2 mg samples were first dissolved in a solution (1:9, v/v) containing Nafion (5%) and water (2 mL) by sonication. Then, 20 µL freshly prepared suspension was dropped on the surface of a prepolished glassy carbon electrode (GCE, 3 mm in diameter) and dried at room temperature before measurements. Before the HER and OER activity tests, cyclic voltammetry (CV) for these electrocatalysts was performed in 1.0 M KOH solution at a scan rate of 50 mV s^{-1} to activate the electrocatalysts. The polarization curves were acquired using linear sweep voltammetry (LSV) for the HER and OER in 1.0 M KOH solution at a sweep rate of 5 mV s⁻¹. *iR* compensation of 95% was applied via electrochemical software. The Tafel plots were derived from the OER and HER polarization curves (1 mV s^{-1}) and constructed using the Tafel equation. The chronopotentiometric (CP) and chronoamperometric (CA) measurements, as well as LSV after 3000 continuous CV cycles were also conducted to evaluate their durability. The electrocatalytic performances toward overall water splitting were measured by employing Co₁Mn₁ NBs and Co₁Mn₁Se NBs as working electrodes for the OER and HER, respectively; the sweep rate was 5 mV s^{-1} . For comparison, an Ir/C (+)//Pt/C (-) couple was also used as the baseline catalyst. It was worth noting that all the potentials measured were calibrated to a reversible hydrogen electrode

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(RHE), and state-of-the-art Ir/C and Pt/C catalysts (20 wt%, 2– 5 nm Pt nanoparticles) purchased from Johnson Matthey (JM) Corporation were also employed as baseline catalysts for all the electrochemical measurements.

3. Results and discussion

The syntheses of CoMn NBs and CoMnSe NBs were carried out through a facile one-step method as illustrated in Scheme 1. The morphologies and microstructures of the as-prepared Co_1Mn_1 NBs are characterized by TEM and SEM. The unique mesoporous nanobundles assembled with abundant ultrathin nanosheets can be clearly observed in the HAADF-STEM images (Fig. 1a and b), which can efficiently provide ion-diffusion routes that enable mass transfer and electron mobility. A clear view also indicates that the mesoporous Co_1Mn_1 NBs are composed of parallelly interconnected nanosheets (Fig. 1c, S1a and S1b†). Also, the two ends of the nanobundle comprise three to five forks generated by a plurality of nanosheets (Fig. 1d and S2†) and form a mesoporous nanobundle-like arrangement, which is also favorable for the mass transfer and ion diffusion.^{36,37}

The HRTEM image was recorded by focusing individual nanobundles to investigate their crystal structure. As seen, the lattice spacing of ca. 0.284 and 0.301 nm was matched well with the d-spacing of the (200) and (112) planes of CoMn NBs (Fig. 1e), respectively, and no obvious continuous lattice fringes can be observed, corroborating the low crystallinity of CoMn NBs.³⁸⁻⁴⁰ The crystal structures of mesoporous Co₁Mn₁ NBs were further confirmed by employing the PXRD technique. As shown in Fig. 1f, the mesoporous Co₁Mn₁ NBs displayed the typical diffraction peaks of CoMn oxides (JCPDS: # 77-0471), while some weak peaks could be indexed to Mn₂O₃.^{41,42} The BET technique has also been employed to deeply investigate the structural features of this nanobundle catalyst. As seen in Fig. S3,[†] the BET surface area of Co_1Mn_1 NBs is 208.3 m² g⁻¹, and the average pore size is about 5.1 nm, suggesting the high surface area and mesoporous properties, which is in accordance with the TEM observations.

For comparison, the TEM images of $Co_1Mn_{0.8}$ NBs, $Co_1Mn_{1.2}$ NBs, and $Co(OH)_2$ were also acquired. As seen in Fig. S4,† both



CoMnSe nanobundles



Fig. 1 (a and b) HAADF-STEM images, (c and d) representative TEM images, (e) HRTEM image and SAED pattern, and (f) PXRD pattern and (g) EDX spectrum of Co_1Mn_1 NBs.

Co₁Mn_{0.8} and Co₁Mn_{1.2} NBs also displayed the typical nanobundle structure similar to Co₁Mn₁ NBs. However, the thicknesses of individual Co₁Mn_{0.8} NBs and Co₁Mn_{1.2} NBs were found to be smaller than that of Co₁Mn₁ NBs, indicating that the feed ratio of precursors plays a significant role in determining the final shapes of the products.⁴³ Apart from these, we have also studied the specific morphology of Co(OH)₂. Differently, Fig. S5† shows that the unique Co(OH)₂ NBs are comprised of many nanosheets that distributed uniformly, and the thickness of the nanobelts is around 30 nm, which is much thinner than that of CoMn NBs. For gaining insight into the composition information of these products, the EDX tests have also been well conducted. As seen in Fig. 1g, the atomic ratio of Co/Mn for Co₁Mn₁ NBs was 47.9 : 52.1, being consistent with

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the feed amount. And the atomic ratios of Co/Mn for Co₁Mn_{0.8} NBs and Co₁Mn_{1.2} NBs were also calculated to be 55.9 : 44.1 and 45.4 : 54.6, respectively (Fig. S4c and S4f[†]), both of which were also greatly in agreement with their feed amounts.

In order to produce effective HER catalysts, we have also successfully constructed the CoMnSe catalysts through the same method. As displayed in Fig. 2a-d, the Co₁Mn₁Se also showed a similar nanobundle morphology assembled by ultrathin nanosheets to Co1Mn1 NBs. To corroborate the phase composition of the as-obtained CoMnSe catalysts, the PXRD patterns have also been obtained. As displayed in Fig. S6,† the PXRD patterns of the Co1Mn1Se NBs showed a slight difference in comparison with Co1Mn1, caused by the dopant Se, demonstrating the successful Se doping. Moreover, we have also prepared the other two types of CoMnSe NBs for comparison. As seen in Fig. S7,† both Co1Mn0.8 R NBs and Co1Mn1.2 Se NBs also possessed a similar morphology to Co1Mn0.8 NBs and Co1Mn1.2 NBs. And the compositions of these three types of electrocatalysts have also been measured; all of them well correspond to the theoretical ratios (Fig. 2e and S7c and S7f⁺). From these results, we can come to a conclusion that the Se introduction



Fig. 2 (a and b) HAADF-STEM, (c and d) representative TEM, (e) SEM-EDX spectrum of Co_1Mn_1Se NBs.

has no effects on the ultimate morphology and structure of the CoMn NBs.

XPS was applied to understand the surface chemical compositions and valences of the resultant Co1Mn1 NBs and Co₁Mn₁Se NBs. Fig. 3a shows the survey spectra of Co₁Mn₁ NBs and Co₁Mn₁Se NBs. It is clearly displayed that the signals of both Co and Mn are clearly observed for both Co1Mn1 NBs and Co₁Mn₁Se NBs. However, for the Co₁Mn₁Se NBs, the Mn, Se, and O signals are remarkably enhanced, confirming the successful incorporation of Mn and Se in Co oxides. Fig. 3b exhibits the Co 2p XPS spectrum of Co₁Mn₁Se NBs; as seen, the obvious peaks at 798.3 and 782.9 eV are corresponded to Co²⁺ $2p_{1/2}$ and $Co^{2+} 2p_{3/2}$, and the peak at 784.5 eV is ascribed to Co^{3+} $2p_{1/2}$, while the other peaks are typical satellite peaks. More importantly, the peak area of Co²⁺ is obviously higher than that of Co³⁺, indicating the presence of oxygen vacancies, which may be key for promoting the overall water splitting performances.44 With regard to Mn 2p, as shown in Fig. 3c, the peaks at 642.3 and 653.9 eV can be assigned to $Mn(\pi)$, while another peak at 654.7 eV is characteristic of Mn(III) cation.^{45,46} As for Se 3d, the XPS spectrum (Fig. 3d) can be well deconvoluted into two peaks at 54.4 and 55.8 eV, being consistent with the Se^{2-} of Se $3d_{5/2}$ and Se $3d_{3/2}$, which may be ascribed to the surface oxidation of the selenide.47,48 These results have indicated the presence of the mixed valence of metal ions $(Mn^{2+}/Mn^{3+} and Co^{2+}/Co^{3+})$ in Co₁Mn₁Se NBs, which is highly expected to play a significant role in the enhancement of electrocatalytic activity.

In consideration of the unique nanobundle structure, the newly generated CoMn NBs are thus highly desirable to obtain excellent electrochemical properties. In this regard, we here conducted the electrochemical measurements to evaluate their OER catalytic properties by selecting state-of-the-art Ir/C and $Co(OH)_2$ NB catalysts for comparison. The OER activity was first assessed using LSV at a scan rate of 5 mV s⁻¹ in 1.0 M KOH solution. Fig. 4a showed the *iR*-compensated LSV curves of these five electrocatalysts. As seen, the Co₁Mn₁ NB electrode exhibits the most excellent activity in comparison with the other four electrocatalysts. From Fig. 4b, we can find that the optimal Co₁Mn₁ NB electrode requires an overpotential of only 221 mV to achieve the current density of 10 mA cm⁻², which is 34, 54, 84, 118, and 195 mV lower than those of Co₁Mn_{1.2} NBs,



Fig. 3 XPS spectra of (a) the survey scan of Co_1Mn_1NBs and Co_1Mn_1Se NBs, (b) Co 2p, (c) Mn 2p, and (d) Se 3d.



Fig. 4 (a) Polarization curves, (b) overpotentials at the current densities of 10 and 100 mA cm⁻², and (c) Tafel slopes of Co_1Mn_1 NBs, $Co_1Mn_{1.2}$ NBs, $Co_1Mn_{0.8}$ NBs, Ir/C, and $Co(OH)_2$ NBs. (d) Polarization curves of Co_1Mn_1 NBs obtained before and after 3000 potential cycles. (e) Prolonged CP of Co_1Mn_1 NBs for 36 h.

Co₁Mn_{0.8} NBs, benchmark Ir/C, Co(OH)₂ NBs, and Mn₂O₃ (Fig. S8†), respectively. What's more, the OER electrocatalytic activity of Co₁Mn₁ NBs is also superior to most of the recently reported binary or ternary electrocatalysts (Table S1†). Furthermore, the optimized Co₁Mn₁ NBs also need only 330 mV to reach a current density of 100 mA cm⁻², which is even 89 mV lower than that of the Ir/C catalyst, further confirming the remarkable OER catalytic activity.

Meanwhile, for assessing the reaction kinetics, the Tafel slopes of these electrocatalysts have also been calculated. As shown in Fig. 4c, the Tafel slope of Co₁Mn₁ NBs was 39.8 mV dec^{-1} , which was considerably lower than those of $Co_1Mn_{1,2}$ NBs (62.2 mV dec⁻¹), Co₁Mn_{0.8} NBs (65.5 mV dec⁻¹), Ir/C (67.8 mV dec⁻¹), and Co(OH)₂ NBs (109.2 mV dec⁻¹), indicating more beneficial OER kinetics for Co1Mn1 NBs.49 Besides the OER activity and kinetics, the durability is also another crucial parameter for evaluating their electrochemical properties. Accordingly, LSV after 3000 continuous CV cycles and prolonged CP test were also conducted to assess their durability. As shown in Fig. 4d, the polarization curve of Co1Mn1 NBs after CV of 3000 cycles is almost overlapped with the original one. Moreover, the overpotential only increases by 32 mV for continuous 18 h CP test (Fig. 4e). And the current densities of Co₁Mn₁ NBs in CA measurements at the overpotentials of 400 and 300 mV only decayed slightly after successive electrolysis for more than 50 000 s (Fig. S9[†]). These results have demonstrated the outstanding electrocatalytic OER durability, which is

significant for practical applications. The electrochemically active surface area (ECSA) has been generally regarded as a crucial factor affecting the electrocatalytic performances of catalysts, which is assumed by capacitance measurements *via* CV in the double layer region at different scan rates (Fig. S10[†]).^{50,51} From Fig. S11,[†] it was found that the ECSA of Co_1Mn_1 NBs was 40 cm⁻², which was 1.14, 1.23, and 1.60 times higher than those of $Co_1Mn_{1.2}$ NBs (35 cm⁻²), $Co_1Mn_{0.8}$ NBs (32.5 cm⁻²), and $Co(OH)_2$ NBs (25 cm⁻²), respectively. The superior OER activity of Co_1Mn_1 NBs can mainly be associated with the high ECSA.⁵²

The electrocatalytic activity of CoMnSe NBs for hydrogen evolution was also investigated in depth. For a good comparison, the HER activities of $Co(OH)_2$ NBs and commercial Pt/C catalysts were also tested. An inspection of the polarization curves indicates that the electrocatalytic activity of these catalysts obey the following sequence: Pt/C > Co_1Mn_1Se NBs > Co_1Mn_{1.2}Se NBs > Co_1Mn_{0.8}Se NBs > Co(OH)_2 NBs (Fig. 5a). For instance, to achieve the current density of 10 mA cm⁻², an overpotential of 87.3 mV is required for Co_1Mn_1Se NBs, which is 34.9, 74.9, and 102.6 mV lower than those of Co_1Mn_{1.2}Se NBs (122.2 mV), Co_1Mn_{0.8}Se NBs (162.2 mV), and Co(OH)_2 NBs (189.9 mV) (Fig. 5b), respectively. Moreover, the electrocatalytic activity of Co_1Mn_1Se NBs also compares favorably to that of many previously reported 3d TM catalysts (Table S2†). More importantly, the current densities of all the electrocatalysts



Fig. 5 (a) Polarization curves, (b) overpotentials at a current density of 10 mA cm⁻², and (c) Tafel slopes of $Co_1Mn_1Se NBs$, $Co_1Mn_{1.2}Se NBs$, $Co_1Mn_{0.8}Se NBs$, Pt/C, and Co(OH)₂ NBs. (d) Polarization curves of Co₁Mn₁Se NBs obtained before and after 3000 potential cycles. (e) Prolonged CP of Co₁Mn₁Se NBs for 18 h.

based on the real surface area are much higher than those based on the projected area (Fig. S12†). Remarkably, the Co_1Mn_1 NBs and Co_1Mn_1 Se NBs require the overpotentials of 210 and 75.6 mV to achieve the current density of 10 mA cm⁻² for the OER and HER, respectively, showing great potential for practical water splitting. Fig. 5c presents the Tafel slopes of these five catalyst-modified electrodes. As seen, the measured Tafel slope of Co_1Mn_1 Se NBs was about 71.2 mV dec⁻¹, which was obviously smaller than those of $Co_1Mn_{1.2}$ Se NBs (93.5 mV dec⁻¹), $Co_1Mn_{0.8}$ Se NBs (132.5 mV dec⁻¹), and $Co(OH)_2$ NBs (192.3 mV dec⁻¹). Additionally, the Tafel slope of Co_1Mn_1 Se NBs falls within the range of 40 to 120 mV dec⁻¹, suggesting that the HER is probably taking place on the surface of Co_1 - Mn_1 Se NBs and proceeding through the Volmer–Heyrovsky mechanism.⁵³

The Co₁Mn₁Se NBs also displayed excellent HER durability, in which negligible electrocatalytic activity degradation was observed after being subjected to CV of 3000 cycles in 1.0 M KOH solution (Fig. 5d). The prolonged CP results also indicated that the overpotential of Co₁Mn₁Se NBs exhibited the negligible increase after continuous HER testing for 36 h (Fig. 5f). Moreover, the CA results also verify that the Co₁Mn₁Se NBs show a very slow decay of current density and maintain 72% and 83% of the initial current at the overpotentials of -200 and -100 mV (Fig. S13†). These results have directly confirmed the outstanding long-term stability of Co₁Mn₁Se NBs for the HER.⁵⁴

Encouraged by the outstanding OER performance of Co1Mn1 NBs, excellent HER performance of Co1Mn1Se NBs in 1.0 M KOH solution, and their potential for practical applications, we here employed Co1Mn1 NBs as the anode and Co1Mn1Se NBs as the cathode to assemble an alkaline electrolyzer for overall water splitting (Fig. 6a).⁵⁵ For comparison, the Ir/C(+)//Pt/C(-)was also constructed and measured in a two-electrode configuration. The Co1Mn1 NBs (+)//Co1Mn1Se NB (-) couple can deliver a water splitting current density of 10 mA cm⁻² by only employing a voltage of 1.60 V (Fig. 6b), outperforming the Ir/C (+)//Pt/C (-) couple (1.62 V) and many previous catalysts (Table S3[†]), which indicates the outstanding electrochemical water splitting activity. Significantly, the Co₁Mn₁ NBs (+)//Co₁- $Mn_1Se NB (-)$ couple can also deliver a larger current density than the Ir/C (+)//Pt/C (-) couple at high potential (Fig. 6c). In detail, the current density of the Co₁Mn₁ NBs (+)//Co₁Mn₁Se NB (-) couple was 189.3 mA cm⁻² at a potential of 1.8 V, which was much higher than that of the Ir/C (+)//Pt/C (–) couple (65.4 mA cm^{-2}), further confirming the excellent electrocatalytic activity. To study the oxygen and hydrogen conversion rates, the faradaic efficiency measurements have also been performed. As seen in Fig. S14a,† the end values of dissolved oxygen are 2.65 and 2.52 for red and black lines, respectively. Therefore, the faradaic efficiency is 95.1%, indicating that the detected oxidation current can be ascribed to the OER process catalyzed by Co1Mn1 NB catalysts. From Fig. S14b,† the faradaic efficiency for hydrogen conversion is 92.3%.^{56,57} Furthermore, the Co₁Mn₁ NBs (+)//Co1Mn1Se NB (-) couple also displays superior longterm stability, where its cell potential has an unobvious variation at the current density of 10 mA cm^{-2} for 36 h (Fig. 6d),



Fig. 6 (a) Illustration of overall water electrolysis. (b) Polarization curves of the Co₁Mn₁ NBs (+)//Co₁Mn₁Se NB (-) couple and Ir/C (+)//Pt/C (-) couple in 1.0 M KOH solution with a scan rate of 5 mV s⁻¹, and (c) current densities of the Co₁Mn₁ NBs (+)//Co₁Mn₁Se NB (-) couple and Ir/C (+)//Pt/C (-) couple at different voltages. (d) Prolonged CP of the Co₁Mn₁ NBs (+)//Co₁Mn₁Se NB (-) couple for 36 h.

suggesting the remarkable durability of electrocatalytic activity toward overall water splitting.

In addition, the morphology and composition of the Co₁-Mn₁Se NBs after long-term CP test are also studied attentively (Fig. S15[†]). Remarkably, the Co₁Mn₁Se NBs could also maintain their unique nanobundle structure and composition with negligible change after the long-term stability test, which was also another piece of evidence confirming their excellent electrocatalytic durability, thus holding great potential for practical applications.⁵⁸ To further study the surface compositions, we have conducted the XPS tests for the Co1Mn1 and Co1Mn1Se NB catalysts after long-term CP testing. As shown in Fig. S16,† both Co₁Mn₁ and Co₁Mn₁Se NBs after long-term CP testing possessed the mixed metal valences (Co2+, Co3+, Mn2+, and Mn³⁺) similar to what was observed in the XPS spectra before CP tests. However, after a detailed observation, we could also find that the XPS spectra of Co 2p showed a peak area increase for Co³⁺, which corresponded to the oxidized Co species during the overall water splitting.59,60 Such a transformation explains the excellent overall water splitting activity of the Co1Mn1 NBs (+)//Co₁Mn₁Se NB (-) couple and is in accordance with the above results.

4. Conclusions

In summary, an advanced class of nanobundle-like CoMn oxides and CoMn selenides with a controlled shape and structure have been successfully constructed through a facile and one-pot hydrothermal method for the first time. The systematic experiments indicated that the Mn incorporation could favourably and significantly modify the electronic structure, shape, and ECSA of Co oxides. Impressively, the CoMn and CoMnSe NBs can exhibit excellent OER and HER activity, and the optimized Co₁Mn₁ NBs and Co₁Mn₁Se NBs need the overpotentials of only 221 and 87.3 mV to achieve the current density of 10 mA cm⁻², respectively, comparable to those of most of the 3d TM electrocatalysts. More importantly, both of them can also display superior long-term stability for at least 36 h at the current density of 10 mA cm⁻². Remarkably, the Se introduction is also favourable for facilitating the bonding between the metal and Se, resulting in the optimal Gibbs free energy for the water electrolysis, and the Co₁Mn₁ NBs (+)//Co₁-Mn₁Se NB (-) couple shows outstanding water electrolysis performances relative to those of Ir/C (+)//Pt/C (-). More interestingly, both CoMn NBs and CoMnSe NBs also possess superior long-term stability with negligible activity and morphological decay in the stability test, serving as promising earth-abundant electrocatalysts for practical water splitting.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- A. Kowal, M. Li, M. Shao, K. Sasaki, M. B. Vukmirovic, J. Zhang, N. S. Marinkovic, P. Liu, A. I. Frenkel and R. R. Adzic, *Nat. Mater.*, 2009, 8, 325–330.
- 2 P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. Yu, Z. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney and A. Nilsson, *Nat. Chem.*, 2010, 2, 454–460.
- 3 S. Linic, P. Christopher and D. B. Ingram, *Nat. Mater.*, 2011, **10**, 911–921.
- 4 L. Fang, W. Li, Y. Guan, Y. Feng, H. Zhang, S. Wang and Y. Wang, *Adv. Funct. Mater.*, 2017, **27**, 1701008.
- 5 M. R. Gao, Y. F. Xu, J. Jiang, Y. R. Zheng and S. H. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 2930–2933.
- 6 D. Y. Chung, S. W. Jun, G. Yoon, H. Kim, J. M. Yoo, K. S. Lee, T. Kim, H. Shin, A. K. Sinha, S. G. Kwon, K. Kang, T. Hyeon and Y. E. Sung, *J. Am. Chem. Soc.*, 2017, **139**, 6669–6674.
- 7 M. Qian, S. Cui, D. Jiang, L. Zhang and P. Du, *Adv. Mater.*, 2017, **29**, 1704075.
- 8 Y. Liu, H. Cheng, M. Lyu, S. Fan, Q. Liu, W. Zhang, Y. Zhi, C. Wang, C. Xiao, S. Wei, B. Ye and Y. Xie, *J. Am. Chem. Soc.*, 2014, **136**, 15670–15675.
- 9 R. Liu, Y. Wang, D. Liu, Y. Zou and S. Wang, *Adv. Mater.*, 2017, **29**, 1701546.
- 10 C. Huang, T. Ouyang, Y. Zou, N. Li and Z.-Q. Liu, *J. Mater. Chem. A*, 2018, **6**, 7420–7427.
- 11 J.-Y. Wang, T. Ouyang, N. Li, T. Ma and Z.-Q. Liu, *Sci. Bull.*, 2018, **63**, 1130–1140.

- 12 R. Subbaraman, D. Tripkovic, K. C. Chang, D. Strmcnik,
 A. P. Paulikas, P. Hirunsit, M. Chan, J. Greeley,
 V. Stamenkovic and N. M. Markovic, *Nat. Mater.*, 2012, 11, 550–557.
- 13 Y. Tang, H. Yang, J. Sun, M. Xia, W. Guo, L. Yu, J. Yan, J. Zheng, L. Chang and F. Gao, *Nanoscale*, 2018, **10**, 10459– 10466.
- 14 K. Liu, F. Wang, T. A. Shifa, Z. Wang, K. Xu, Y. Zhang, Z. Cheng, X. Zhan and J. He, *Nanoscale*, 2017, 9, 3995–4001.
- 15 H. Cheng, M.-L. Li, C.-Y. Su, N. Li and Z.-Q. Liu, *Adv. Funct. Mater.*, 2017, **27**, 1701833.
- 16 A. S. Schenk, S. Eiben, M. Goll, L. Reith, A. N. Kulak, F. C. Meldrum, H. Jeske, C. Wege and S. Ludwigs, *Nanoscale*, 2017, 9, 6334–6345.
- 17 A. Yu, C. Lee, M. H. Kim and Y. Lee, ACS Appl. Mater. Interfaces, 2017, 9, 35057–35066.
- 18 L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang and L. Dai, Angew. Chem., 2016, 55, 5277–5281.
- 19 X. Ma, J. Wen, S. Zhang, H. Yuan, K. Li, F. Yan, X. Zhang and Y. Chen, ACS Sustainable Chem. Eng., 2017, 5, 10266–10274.
- 20 T. Ouyang, A. N. Chen, Z. Z. He, Z. Q. Liu and Y. Tong, *Chem. Commun.*, 2018, **54**, 9901–9904.
- 21 J. X. Feng, L. X. Ding, S. H. Ye, X. J. He, H. Xu, Y. X. Tong and G. R. Li, *Adv. Mater.*, 2015, **27**, 7051–7057.
- 22 Y. Sun, L. Hang, Q. Shen, T. Zhang, H. Li, X. Zhang, X. Lyu and Y. Li, *Nanoscale*, 2017, **9**, 16674–16679.
- 23 J. Shen, M. Wang, L. Zhao, J. Jiang, H. Liu and J. Liu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 8786–8796.
- 24 J. Chi, H. Yu, B. Qin, L. Fu, J. Jia, B. Yi and Z. Shao, ACS Appl. Mater. Interfaces, 2017, 9, 464–471.
- 25 D. Chen, C. L. Dong, Y. Zou, D. Su, Y. C. Huang, L. Tao, S. Dou, S. Shen and S. Wang, *Nanoscale*, 2017, 9, 11969– 11975.
- 26 L. Ai, T. Tian and J. Jiang, *ACS Sustainable Chem. Eng.*, 2017, 5, 4771–4777.
- 27 H. Schäfer and M. Chatenet, *ACS Energy Lett.*, 2018, **3**, 574–591.
- 28 R. Li, D. Zhou, J. Luo, W. Xu, J. Li, S. Li, P. Cheng and D. Yuan, *J. Power Sources*, 2017, 341, 250–256.
- 29 L. Zhuang, L. Ge, Y. Yang, M. Li, Y. Jia, X. Yao and Z. Zhu, *Adv. Mater.*, 2017, **29**, 1606793.
- 30 J. Deng, H. Zhang, Y. Zhang, P. Luo, L. Liu and Y. Wang, J. Power Sources, 2017, 372, 46–53.
- 31 C. Huang, T. Ouyang, Y. Zou, N. Li and Z.-Q. Liu, *J. Mater. Chem. A*, 2018, **6**, 7420–7427.
- 32 K. Xiao, L. Zhou, M. Shao and M. Wei, *J. Mater. Chem. A*, 2018, **6**, 7585–7591.
- 33 M. Zheng, J. Du, B. Hou and C.-L. Xu, ACS Appl. Mater. Interfaces, 2017, 9, 26066–26076.
- 34 S. H. Ahn and A. Manthiram, J. Mater. Chem. A, 2017, 5, 2496–2503.
- 35 H. Cheng, C.-Y. Su, Z.-Y. Tan, S.-Z. Tai and Z.-Q. Liu, *J. Power Sources*, 2017, **357**, 1–10.
- 36 V. Malgras, H. Ataee-Esfahani, H. Wang, B. Jiang, C. Li,
 K. C. Wu, J. H. Kim and Y. Yamauchi, *Adv. Mater.*, 2016, 28, 993–1010.

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- 37 Q. Xu, H. Jiang, H. Zhang, H. Jiang and C. Li, *Electrochim. Acta*, 2018, **259**, 962–967.
- 38 X. Kong, T. Zhu, F. Cheng, M. Zhu, X. Cao, S. Liang, G. Cao and A. Pan, ACS Appl. Mater. Interfaces, 2018, 10, 8730–8738.
- 39 J. Zhao, J. Chen, S. Xu, M. Shao, D. Yan, M. Wei, D. G. Evans and X. Duan, *J. Mater. Chem. A*, 2013, **1**, 8836.
- 40 H. Xu, P. Song, C. Fernandez, J. Wang, M. Zhu, Y. Shiraishi and Y. Du, ACS Appl. Mater. Interfaces, 2018, 10, 12659–12665.
- 41 L. Hu, H. Zhong, X. Zheng, Y. Huang, P. Zhang and Q. Chen, *Sci. Rep.*, 2012, **2**, 986.
- 42 H. Xu, J. Wei, K. Zhang, Y. Shiraishi and Y. Du, *ACS Appl. Mater. Interfaces*, 2018, **10**, 29647–29655.
- 43 G.-R. Xu, J. Bai, J.-X. Jiang, J.-M. Lee and Y. Chen, *Chem. Sci.*, 2017, **8**, 8411–8418.
- 44 Y. Pi, Q. Shao, P. Wang, F. Lv, S. Guo, J. Guo and X. Huang, Angew. Chem., 2017, 56, 4502–4506.
- 45 R. Frydendal, L. C. Seitz, D. Sokaras, T.-C. Weng,
 D. Nordlund, I. Chorkendorff, I. E. L. Stephens and
 T. F. Jaramillo, *Electrochim. Acta*, 2017, 230, 22–28.
- 46 J.-G. Wang, Y. Yang, Z.-H. Huang and F. Kang, J. Mater. Chem., 2012, 22, 16943.
- 47 T. Chen and Y. Tan, Nano Res., 2018, 11, 1331-1344.
- 48 Z. Gao, J. Qi, M. Chen, W. Zhang and R. Cao, *Electrochim. Acta*, 2017, **224**, 412–418.
- 49 X. Tian, Y. Liu, D. Xiao and J. Sun, *J. Power Sources*, 2017, **365**, 320–326.

- 50 H. Xu, K. Zhang, B. Yan, J. Wang, C. Wang, S. Li, Z. Gu, Y. Du and P. Yang, *J. Power Sources*, 2017, **356**, 27–35.
- 51 Y. Zhang, Q. Shao, S. Long and X. Huang, *Nano Energy*, 2018, **45**, 448–455.
- 52 H. Xu, B. Yan, S. Li, J. Wang, P. Song, C. Wang, J. Guo and Y. Du, *J. Power Sources*, 2018, **384**, 42–47.
- 53 G.-F. Chen, T. Y. Ma, Z.-Q. Liu, N. Li, Y.-Z. Su, K. Davey and S.-Z. Qiao, *Adv. Funct. Mater.*, 2016, **26**, 3314–3323.
- 54 H. Xu, B. Yan, S. Li, J. Wang, C. Wang, J. Guo and Y. Du, *Chem. Eng. J.*, 2018, **334**, 2638–2646.
- 55 L. Yu, J. F. Yang, B. Y. Guan, Y. Lu and X. W. D. Lou, *Angew. Chem.*, 2018, **57**, 172–176.
- 56 H. Schäfer, D. M. Chevrier, K. Kuepper, P. Zhang, J. Wollschlaeger, D. Daum, M. Steinhart, C. Heß, U. Krupp, K. Müller-Buschbaum, J. Stangl and M. Schmidt, *Energy Environ. Sci.*, 2016, 9, 2609–2622.
- 57 H. Schäfer, S. Sadaf, L. Walder, K. Kuepper, S. Dinklage, J. Wollschläger, L. Schneider, M. Steinhart, J. Hardege and D. Daum, *Energy Environ. Sci.*, 2015, 8, 2685–2697.
- 58 H. Xu, J. Wei, C. Liu, Y. Zhang, L. Tian, C. Wang and Y. Du, J. Colloid Interface Sci., 2018, 530, 146–153.
- 59 H. Xu, P. Song, C. Liu, Y. Zhang and Y. Du, *J. Colloid Interface Sci.*, 2018, **530**, 58–66.
- 60 L. Jiao, Y. Zhou and H. Jiang, Chem. Sci., 2016, 7, 1690-1695.