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Non-noble metal electrocatalysts have recently received increasing attention for the hydrogen evolution reaction (HER) in acidic electrolytes. However, in alkaline electrolyzers, the slow kinetics of water splitting leads to their poor HER activities. Here, we demonstrate the synthesis of novel hierarchical nanotubes of CoS/MoS₂ and Co₃S₄/MoS₂/Ni₂P which exhibit prominent and durable HER capabilities in alkaline solution. Particularly, the Co₃S₄/MoS₂/Ni₂P nanotubes present an onset overpotential of 60 mV, a Tafel slope of 98 mV dec⁻¹, and a high exchange current density of 0.21 mA cm⁻², which are superior to those exhibited by many noble-metal-free electrocatalysts. The enhanced HER properties of the hybrid nanotubes could be related to their open hollow structure, large surface area and active site number, as well as the synergetic cooperation between different components. The results reported here may provide new inspirations for the construction of advanced nanostructures for promising catalytic applications.

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Introduction

With the depletion of fossil fuels and increasing energy demands, hydrogen (H₂) is widely recognized as a promising energy carrier to meet future energy needs due to its high energy density and environmental friendliness.¹ To produce H₂, water electrolysis by renewable electricity (converted from clean solar energy, wind energy, water energy, and so on) is an important pathway for realizing long-term sustainability.² For the electrocatalytic hydrogen evolution reaction (HER), noble metals especially Pt and its alloys are known as highly efficient electrocatalysts,³ but the high cost and scarcity have greatly impeded their widespread applications.⁴ Recently, transition metal chalcogenides and phosphides have been reported to exhibit high reactivities for the HER in acidic electrolytes.⁵ However, the electrocatalytic HER in alkaline media is less studied,⁶ and the sluggish water dissociation kinetics of electrocatalysts in alkaline solution⁷ usually results in poor HER activities. Therefore, in order to advance the H₂ production efficiency of economical alkaline electrolyzers, searching for

earth-abundant, highly active, and durable electrocatalysts is quite necessary but challenging.

As two important classes of low-dimensional nanomaterials, one-dimensional (1D) and two-dimensional (2D) nanostructures are among the hottest topics of research owing to their exceptional electrical, catalytic, and optical properties.⁸ Nevertheless, for catalysis, highly crystallized 1D nanocrystals (such as nanowires, nanorods, and nanotubes) generally possess a low surface area;⁹ meanwhile, 2D nanosheets have a tendency of restacking and aggregation (unfavorable for the sufficient exposure of active sites),¹⁰ both of which are detrimental to the enhancement of catalytic reactivity. By contrast, integrating 1D and 2D nanomaterials to form a 1D hierarchical nanostructure with vertically grown nanosheets and a porous/hollow interior will be of great interest; these 1D hierarchical nanostructures possess features including a large surface area, low density, and favorable open structure for the penetration and diffusion of reactants.¹¹ Some reports have demonstrated this kind of 1D hierarchical architecture to show remarkable catalytic properties.¹² However, the related research activities have been quite deficient so far. In addition, it is worth mentioning that these nano-architectures enable us to freely construct heterostructures with selected components for versatile functionalities and to further optimize or modify their surface and interface structures as well as composition towards more outstanding performances.

In this work, we for the first time prepared hierarchical porous CoS nanotubes, assembled with hexagonal nanosheets by using a template-assisted approach, which were then used as the growth substrate for further constructing bi-composite CoS/

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† Electronic supplementary information (ESI) available: Details about the preparation, characterization, and electrochemical measurements together with analysis of the morphology, structure, composition, and electrocatalytic activity of the catalysts. See DOI: 10.1039/c7ta08760h

MoS₂ and tri-composite Co₃S₄/MoS₂/Ni₂P hybrid nanotubes. These composite nanotubes displayed excellent activity and stability towards the HER in alkaline electrolytes. In particular, the Co₃S₄/MoS₂/Ni₂P nanotubes exhibit desirable features which make them a promising electrocatalyst: an onset overpotential of 60 mV, a Tafel slope of 98 mV dec⁻¹, and a high exchange current density of 0.21 mA cm⁻². Such types of hybrid nanotubes composed of transition metal chalcogenides and phosphides are promising candidates as low-cost, efficient catalysts for alkaline electrolyzers.

Results and discussion

The synthesis of CoS/MoS₂ (CMS) nanotubes (NTs) was carried out with a template-directed strategy. Initially, Co(OH)_x(CO₃)_y nanowires (Fig. S1†) were prepared by an oleylamine-assisted hydrothermal method,¹³ and were then used as the sacrificial template in the solvothermal formation of CoS nanosheet-assembled hierarchical NTs. After that, the CoS NTs were employed as the growth substrate for the subsequent hybridization of MoS₂ nanosheets (NSs). The X-ray diffraction (XRD) patterns of MoS₂ NSs, CoS NTs and their composites with different MoS₂ loading amounts are shown in Fig. 1a. We can see that the diffraction peaks of CoS are obvious in all hybrids, while the signals of MoS₂ could only be found at higher composition levels such as CMS40 and CMS60, which is probably due to the smaller loading of MoS₂ NSs and their weak crystallinity (broadened diffraction peaks). The diffraction peaks of CoS in pure CoS NTs and CMS NTs are in good agreement with that of hexagonal CoS (JCPDS No. 65-3418). Notably, in comparison with the pristine 2H-MoS₂ phase (JCPDS No. 75-1539), the (002) diffraction peak of our synthesized MoS₂ NSs moved evidently to a position lower than 10°, which indicates that an expanded lamellar structure was formed in our MoS₂ NSs.¹⁴ Correlatively, the schematic unit cell structures of CoS and MoS₂ references are given as the insets accordingly. In addition to the XRD results, the Raman spectra (Fig. 1b) also reveal that the formation of CoS (E_g 460, F_{2g} 505, and A_{1g} 662 cm⁻¹)¹⁵ and MoS₂ (E_{2g} 377 cm⁻¹ and A_{1g} 403 cm⁻¹)¹⁶ in individual NTs and NSs as well as their composites (take CMS60 for example here) occurs. Interestingly, the Mo–O vibrations (B_{2g} 282 cm⁻¹ and B_{1g} 334 cm⁻¹)¹⁷ are detected in both MoS₂ NSs and CoS/MoS₂ NTs, suggesting that the produced MoS₂ NSs with an expanded layer spacing are accompanied by the incorporation of oxygen into the crystal structure. Scanning electron microscopy (SEM) observations of CMS40 in Fig. 1c and d demonstrate that MoS₂ NSs were grown vertically on the surface of tubular CoS backbones. The NTs in the substrate display a primary diameter of 110–150 nm and a length of about 2–5 μm (Fig. 2), while the grown NSs possess a thickness of 2–5 nm and a width of about 30 nm (Fig. 1d and 3). The hollow interiors of CoS/MoS₂ NTs were further confirmed by transmission electron microscopy (TEM) measurements. As shown in Fig. 1e and 2, the CoS NSs (a thickness of 6–10 nm and a width of about 50 nm) and MoS₂ NSs are interconnected with each other to form a shell with high contrast compared to the hollow center. High-resolution TEM (HRTEM) analyses of CMS40 are exhibited in Fig. 1f. The lattice

spacing of 0.29 nm could be attributed to the {100} facets (equivalent to {10 $\bar{1}$ 0} facets) of hexagonal CoS, while the enlarged interlamellar spacing of 0.95 nm is identified as the {002} planes of 2H-MoS₂. Meanwhile, it is worth mentioning that there are plenty of defects such as dislocations and distortions (highlighted in the purple dashed circles) present in both the basal plane and the cross section of the coupled MoS₂ NSs. Noticeably, the dark-field scanning TEM (STEM) graph and corresponding energy dispersive X-ray (EDX) elemental mapping results of CMS40 NTs are disclosed in Fig. 1g, which distinctly evidence the tubular distribution of Co, Mo, S, and O ingredients.

A TEM photo of pure CoS NTs is exhibited in Fig. 2a, from which one can see that the nanotubes in the substrate have a primary diameter of 110–150 nm and a length of about 2–5 μm. Fig. 2b displays one single nanotube with a higher amplification, in which the hollow hierarchical tubular structure and the assembled hexagonal NSs are demonstrated obviously. An elemental line-scanning along the cross section of a nanotube was performed and the results are given in Fig. 2b (inset), which suggest that the elements of Co and S are distributed in a tube-like manner. Moreover, the corresponding STEM graph and EDX elemental mapping results of the nanotube also manifest the distribution of Co and S throughout the whole nanotube. HRTEM images of the CoS nanotube are presented in Fig. 2c and d. Based on the FFT analysis of a hexagonal nanosheet (Fig. 2c), the crystal lattices can be attributed to the [001] diffraction. Therefore, the basal planes of the CoS nanosheet perpendicular to the [001] zone axis are fixed as {001} (equivalent to {0001}), while the six lateral facets parallel to the direction of the electron beam could be ascribed to the {100} planes (equivalent to {0110} facets). In agreement with the FFT result, the basal planes of CoS NSs are determined as {001} (equivalent to {0001}) when considering the lattice spacing of a standing nanosheet (Fig. 2d). To make it clear, the atomic structures of lying and erect NSs as well as a unit cell of CoS are illustrated accordingly (on the right side of Fig. 2d).

The TEM picture of individual MoS₂ NSs shown in Fig. 3a exhibits that the NSs have a small thickness of about 3–5 nm along with a lateral size of around 35 nm and they stack with each other into a lot of bigger aggregates. Fig. 3b shows the HRTEM image of the NSs, where an expanded interlayer spacing of 0.95 nm is identified and it corresponds to the (002) plane of 2H-MoS₂. In addition, a large number of defects (highlighted with yellow dashed lines) including distortions and dislocations of the crystal lattices can be found in both the basal face and the cross section of the NSs. On the basis of the FFT result from a periodic area of the lying nanosheet, the lattice fringes could be indexed to the [001] diffraction. Therefore, the basal planes of MoS₂ NSs can be determined as {001} facets (equivalent to {0001} facets). For elucidation, the schematic structures of a unit cell and [001]-oriented MoS₂ monolayer with O-incorporation are given accordingly (on the right side of Fig. 3b). Furthermore, the STEM image and corresponding EDX elemental mapping results of MoS₂ NSs are provided to confirm the uniform distribution of Mo, S, and O elements.

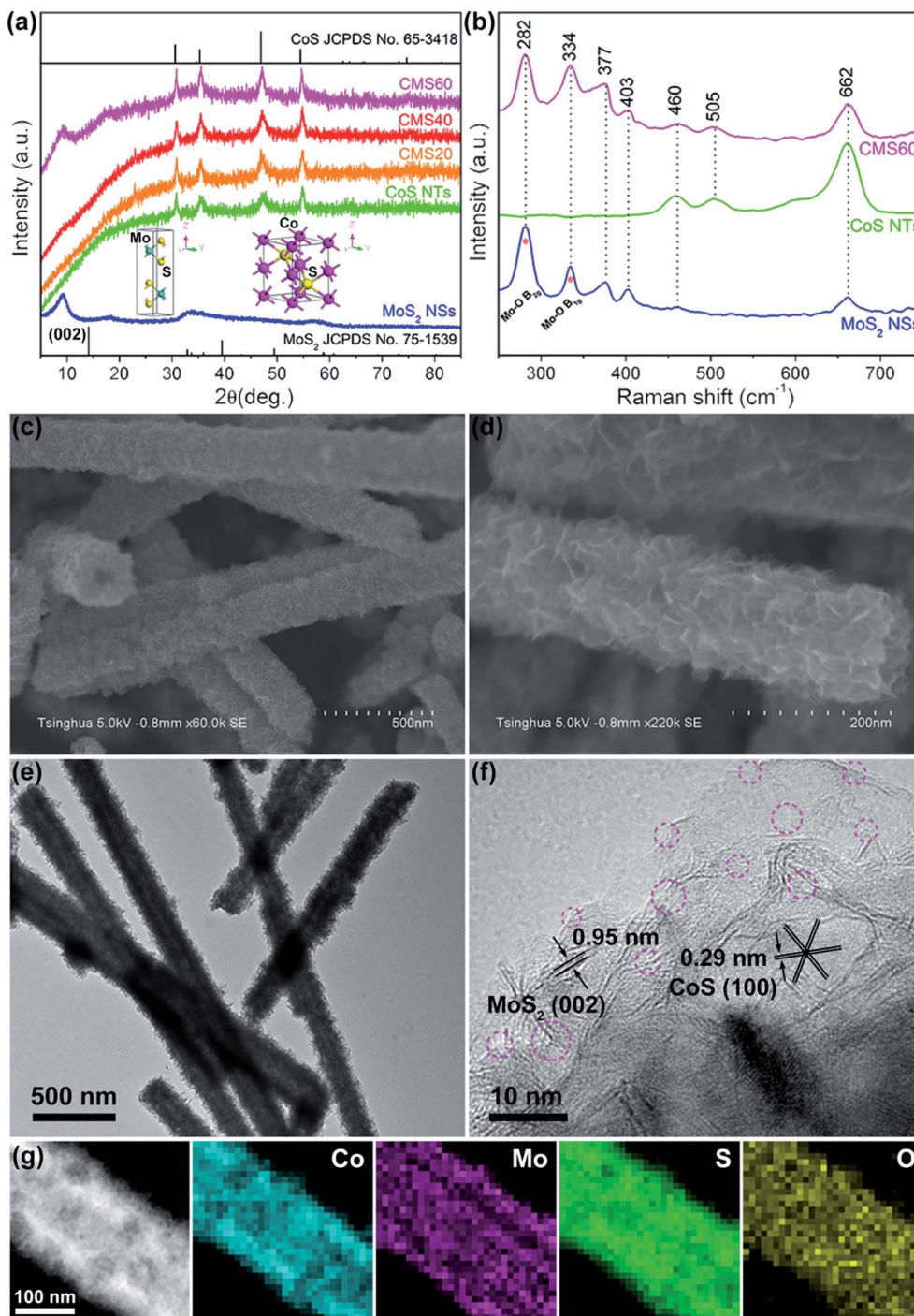


Fig. 1 (a) XRD patterns of MoS₂ nanosheets, CoS nanotubes, and CoS/MoS₂ nanotubes with different MoS₂ contents (CMS20, CMS40, and CMS60 correspond to the calculated MoS₂ loading amount of 20 wt%, 40 wt%, and 60 wt%, respectively). (b) Raman spectra of MoS₂ nanosheets, CoS nanotubes, and CoS/MoS₂ nanotubes. The wavelength of excitation light is 532 nm. (c, d, e, f, and g) are the SEM, TEM and HRTEM, as well as STEM and corresponding EDX mapping results of CoS/MoS₂ nanotubes.

The formation process of CoS nanosheet-assembled hierarchical NTs was investigated by recording the morphologies of products at different reaction stages. We can see that the original Co(OH)_x(CO₃)_y nanowire precursor has a major diameter of 90–120 nm and a length of about 5–6 μm (Fig. 4a and S1†). After reaction for 30 min, lots of small particles started to appear on

the surface of the nanowires (Fig. 4b). When the reaction was suspended at 40 min, the particles outside the nanowire template gradually developed into bigger NSs and a core-shell structure was formed (Fig. 4c). Based on the XRD results of intermediates (Fig. S2†), the shell wrapping the precursor could be determined as the CoS component. Furthermore, when we

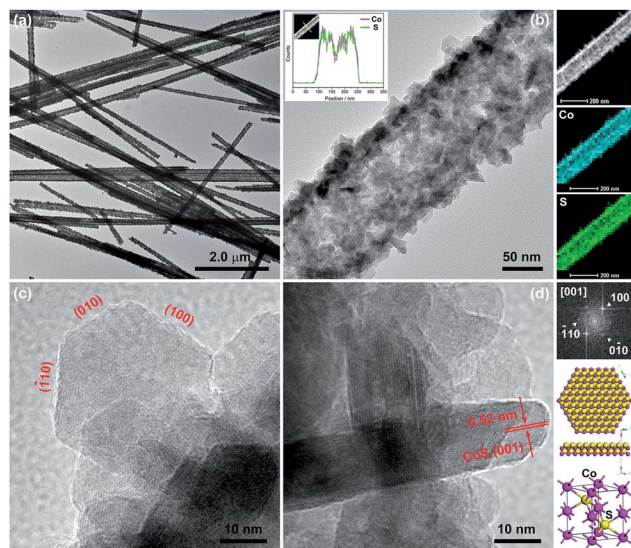


Fig. 2 (a, b) TEM and (c, d) HRTEM images of the CoS nanosheet-assembled nanotubes. The corresponding STEM and EDX elemental line-scanning and mapping results are provided as the insets of (b). Meanwhile, a FFT result as well as pictorial atomic structures of the unit cell and a hexagonal nanosheet of CoS are given as the insets of (d).

extended the reaction time up to 12 h, the precursor was completely decomposed and well-defined porous NTs composed of CoS NSs were obtained (Fig. 4d and 2). During the solvothermal sulfidation course, S^{2-} ions were generated through the alcoholysis of thiourea,^{11a} which then reacted with Co^{2+} ions released from the $Co(OH)_x(CO_3)_y$ precursor to yield CoS under high-temperature conditions. The relational reaction can be expressed as the following equations:

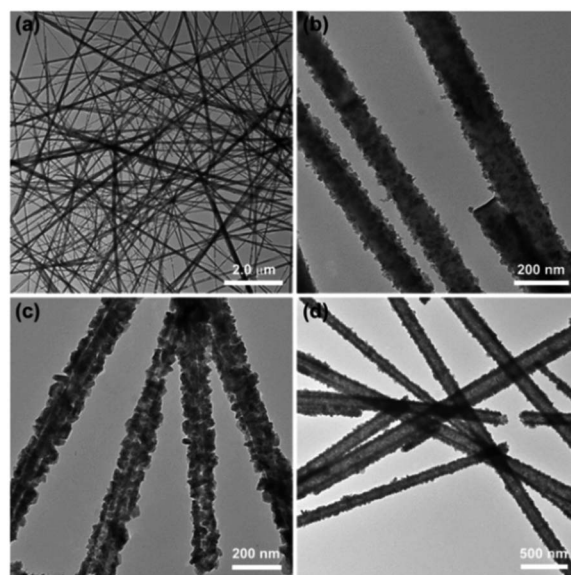
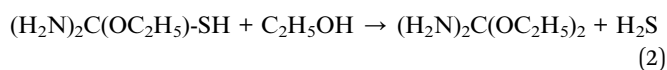
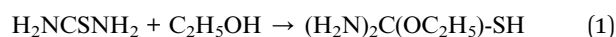
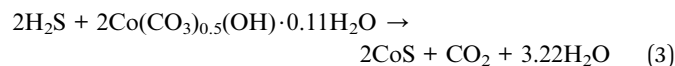


Fig. 4 TEM graphs of products in the formation course of CoS hierarchical nanotubes collected after reaction for (a) 0 min, (b) 30 min, (c) 40 min, and (d) 12 h.



At the early stage of the reaction, S^{2-} ions combined with Co^{2+} ions to form a thin layer of CoS coating on the surface of the precursor, which can serve as a physical barrier to hinder the direct chemical reaction between S^{2-} and inner Co^{2+} ions. The ionic radius of S^{2-} (184 pm) is remarkably bigger than that of Co^{2+} (74 pm). Therefore, in the subsequent reaction procedure, the inward diffusion of S^{2-} through the sulfide layer could be much slower as compared to the outward diffusion of Co^{2+} . Consequently, as the reaction proceeded further, the Co^{2+} from $Co(OH)_x(CO_3)_y$ will preferentially pass through the sulfide shell

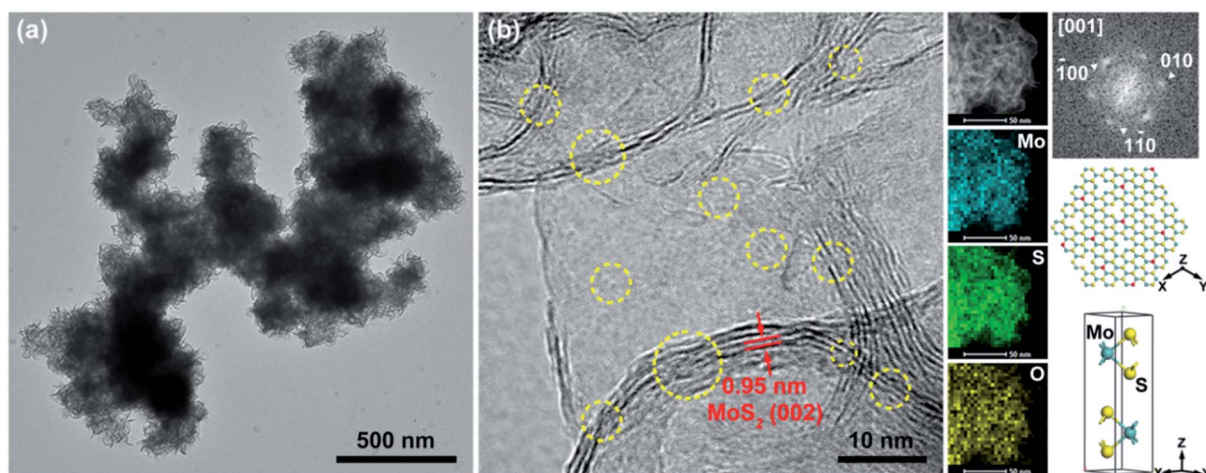


Fig. 3 (a) TEM, (b) HRTEM, and STEM and EDX elemental mapping results of MoS₂ nanosheets. For elucidation, a FFT result as well as the schematic atomic structures of the unit cell and an O-doped monolayer of MoS₂ are also demonstrated.

to integrate with S^{2-} on the outer surface, and finally the NTs were produced with the full dissolution of the central nanowire precursor.

The proposed growth mechanism for the formation of CoS nanosheet-assembled NTs is illustrated in Fig. 5a. In order to achieve an integrative and synergic enhancement in the performance and multiple functionalities, the CoS NTs were further modified to construct heterostructures with selected components. As shown in Fig. 5b, bi-component CMS hybrid NTs can be obtained after MoS_2 was grown onto the surface of the CoS NT substrate. Moreover, a tri-component $Co_3S_4/MoS_2/Ni_2P$ (PN-CMS40) composite could also be synthesized through the phosphorization of $CoS/MoS_2/Ni(OH)_2$ (Fig. S6†) pre-fabricated under hydrothermal conditions.

The XRD patterns of $CoS/MoS_2/Ni(OH)_2$ NTs and PN-CMS40 NTs are displayed in Fig. 6c. For $CoS/MoS_2/Ni(OH)_2$ NTs, the composite presents signals corresponding to hexagonal CoS (JCPDS No. 65-3418) and $Ni(OH)_2$ (JCPDS No. 02-1112), while the spectrum of PN-CMS40 NTs is composed of diffraction peaks belonging to cubic Co_3S_4 (JCPDS No. 11-0121) and hexagonal Ni_2P (JCPDS No. 65-9706). It can be seen from the XRD results that after the hydrothermal growth of $Ni(OH)_2$ on CoS/MoS_2 NTs, the phase of CoS was well preserved (Fig. 1a and 6c). Nevertheless, the XPS analyses (Fig. 7a and S7b†) show that after the hydrothermal reaction, the $Co^{2+}/(Co^{2+} + Co^{3+})$ on the surface is increased from ca. 50% for CoS/MoS_2 NTs to about 85% for $CoS/MoS_2/Ni(OH)_2$ NTs, which may result from the surface reduction of CoS under hydrothermal conditions due to the presence of reducing agents (sodium citrate and hexamethylenetetramine). Interestingly, the CoS was transformed into Co_3S_4 (Fig. 6c) after the phosphorization of $CoS/MoS_2/Ni(OH)_2$ NTs under 350 °C calcination conditions. Meanwhile, through phosphorization, the $Ni(OH)_2$ was changed to Ni_2P (Fig. 6c), which is in good agreement with previous work on the preparation of transition metal phosphides.¹⁸ According to the

HRTEM data (Fig. S6b† and 6b) and XPS spectra (Fig. S7 and S9†), even though MoS_2 existed in both $CoS/MoS_2/Ni(OH)_2$ and PN-CMS40 NT hybrids, the XRD diffraction peaks are hard to be distinguished owing to the lower crystallinity and loading amount of the ultrathin MoS_2 NSs. Fig. 6a shows the TEM image of PN-CMS40 NTs, in which complex NTs with a rough surface can be found. The detailed composition of PN-CMS40 was further studied by HRTEM analyses as shown in Fig. 6b. The MoS_2 NSs show an interlayer spacing of 0.95 nm, which is consistent with the (002) plane of expanded 2H- MoS_2 NSs. Similar to the individual MoS_2 NSs, the MoS_2 in PN-CMS40 is also endowed with a large number of defects as marked by the purple dashed circles. The fast Fourier transformation (FFT) result of the particle lattices highlighted in a yellow dashed circle is given as the inset of Fig. 6b, in which the lattice fringes can be indexed to the [001] diffraction of hexagonal Ni_2P . In addition, lattices with a spacing of about 0.548 nm are discovered, and originate from the occurrence of cubic Co_3S_4 . The dark-field STEM image and corresponding EDX elemental mapping results of a single PN-CMS40 NT are given in Fig. 6d, in which the elemental distribution of Co, Mo, Ni, S, and P is demonstrated clearly.

To comprehend the interaction between different components, as well as the related surface composition and chemical valences of hybrid NTs, X-ray photoelectron spectroscopy (XPS) spectra were collected correspondingly. Here, CMS40 NTs are taken as a typical example. In accordance with the fitting results, for the Co element in pure CoS NTs, the major Co 2p_{3/2} and Co 2p_{1/2} binding energies are located at 778.3 and 793.4 eV, respectively, which could be related to Co^{3+} species,¹⁹ coming probably from the partial surface oxidation of CoS. Meanwhile, the adjacent doublet of 780.4 and 796.3 eV can be attributed to the Co^{2+} state.^{19a,20} Regarding the Mo element in single MoS_2 NSs, the main Mo 3d_{5/2} and Mo 3d_{3/2} peaks around 228.6 and 231.8 eV are due to the presence of the Mo^{4+} chemical state,²¹ while the Mo 3d signals found at 229.4 and 232.7 eV confirm the formation of the Mo^{5+} component,²² which may result from the incorporation of oxygen. By comparison, after MoS_2 was hybridized with CoS to produce CMS NTs, the binding energies of Co 2p in CMS40 are moved to higher positions by 0.3 eV with respect to that in pure CoS NTs. In contrast, the Mo 3d spectrum of CMS40 shows a red-shift of ca. 0.2 eV when compared with that of individual MoS_2 NSs. What's more, on the Pauling scale, the electronegativity value of Mo is 2.16, which is higher than 1.88 for Co. Therefore, after CoS was combined with MoS_2 , the electrons will transfer from CoS to MoS_2 and the formation of a heterojunction and Co–S–Mo bonds at the interfaces could be anticipated. Agreeing well with the Raman results (Fig. 1b), the presence of Mo–O bonds in pure MoS_2 NSs and CMS hybrid NTs is also verified by the Mo 3d (ca. 235.2 eV, Fig. 7b)²³ and O 1s spectra. As shown in Fig. 7c and d, the O 1s spectra of MoS_2 NSs and CMS hybrid NTs consist of a signal located at ca. 530.2 eV, which corresponds to the binding energy of oxygen in $Mo^{(IV)}O_2$.²⁴ Therefore, the $Mo^{(IV)}-O$ bonds are present in the MoS_2 component of both individual NSs and their composite NTs, confirming that the oxygen in MoS_2 is incorporated into the layer structure instead of being introduced by surface

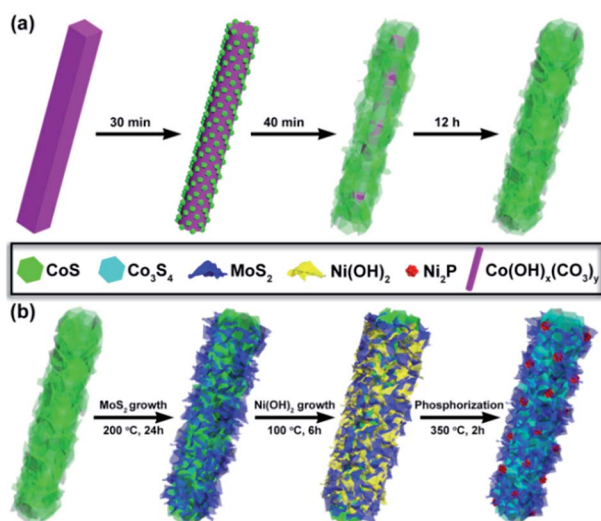


Fig. 5 Schematic exhibiting the evolution processes of (a) CoS nanosheet-assembled nanotubes and (b) bi-component CoS/MoS_2 and tri-component $Co_3S_4/MoS_2/Ni_2P$ hybrid nanotubes.

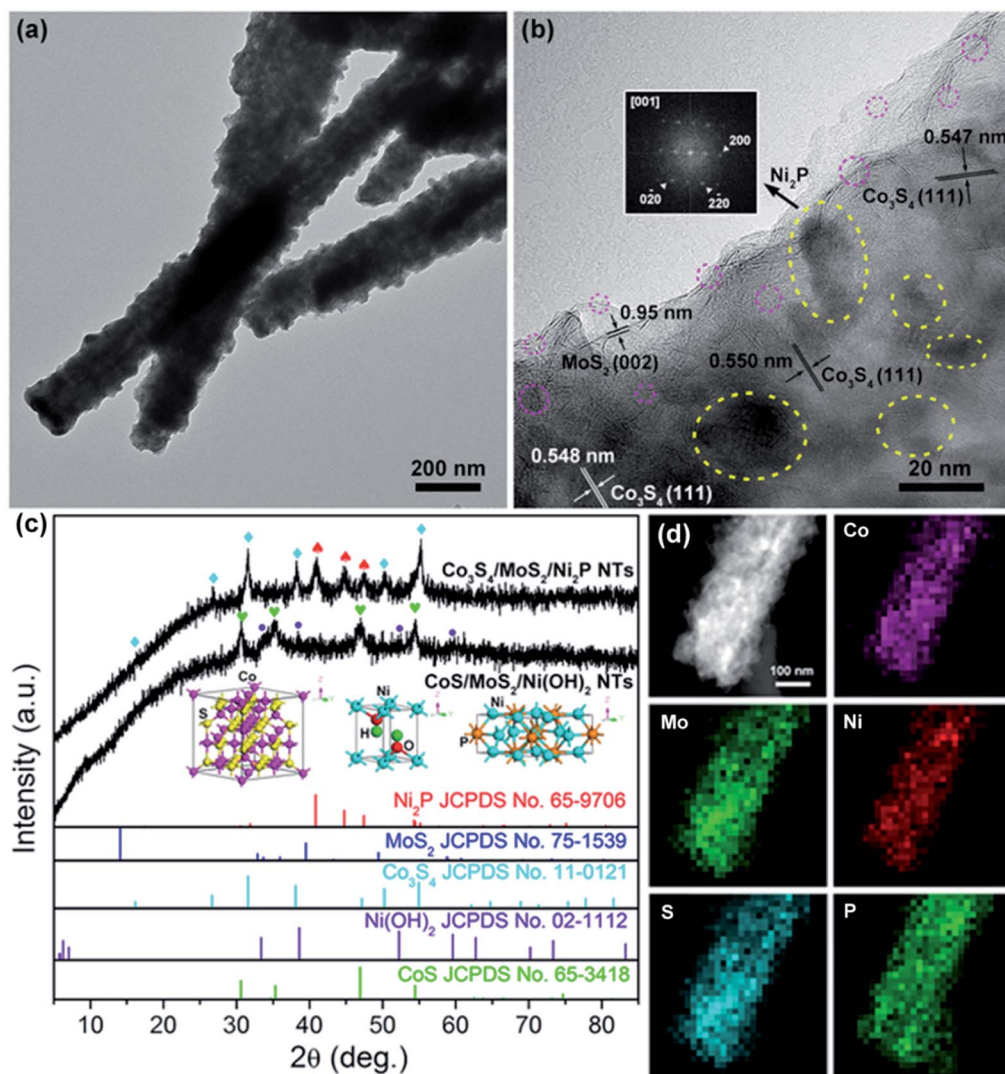


Fig. 6 Typical (a) TEM and (b) HRTEM images of the $\text{Co}_3\text{S}_4/\text{MoS}_2/\text{Ni}_2\text{P}$ nanotubes. The XRD patterns of (c) $\text{CoS}/\text{MoS}_2/\text{Ni}(\text{OH})_2$ and $\text{Co}_3\text{S}_4/\text{MoS}_2/\text{Ni}_2\text{P}$ as well as (d) STEM and corresponding EDX elemental mapping results of the $\text{Co}_3\text{S}_4/\text{MoS}_2/\text{Ni}_2\text{P}$ nanotubes are also presented.

oxidation.¹⁴ Actually, the oxygen-doped MoS_2 NSs can be obtained with preparation temperatures lower than 200 °C,¹⁴ which cause an insufficient reaction process for the remaining Mo–O bonds to be inherited from the molybdate precursors, resulting in the oxygen incorporation into the prepared MoS_2 NSs. Thus, from a synthesis perspective, the O element doping in MoS_2 of our work is also feasible. Moreover, the S 2p XPS spectra of CoS NTs, MoS_2 NSs, and CMS40 NTs, as well as the O 1s XPS signal of CoS NTs can also be found in Fig. S8.† On the other hand, the detailed valence state information on elements in $\text{CoS}/\text{MoS}_2/\text{Ni}(\text{OH})_2$ NTs and $\text{Co}_3\text{S}_4/\text{MoS}_2/\text{Ni}_2\text{P}$ NTs could be achieved from the XPS spectra which are shown in Fig. S7 and S9,† respectively.

The electrocatalytic activities of bi-component CMS NT and tri-component PN-CMS40 NT hybrids for the HER were evaluated in 1.0 M KOH solution. A three-electrode setup was used, in which a graphite rod and saturated calomel electrode were the counter electrode and reference electrode, respectively. From

the linear sweep voltammetry (LSV) curves shown in Fig. 8a, it can be found that the commercial C has a negligible activity for the HER. In comparison with individual MoS_2 NSs and CoS NTs, the HER activities of bi-component CMS NTs with varying MoS_2 contents are dramatically enhanced. The overpotential at 10 mA cm^{-2} (η_{10}) is decreased from 393 mV for MoS_2 NSs and 345 mV for CoS NTs, to 286 mV for CMS20 NTs, 253 mV for CMS60 NTs, and 214 mV for CMS40 NTs. Interestingly, the η_{10} is further notably lowered to 178 mV when the tri-component PN-CMS40 NTs were employed as the catalyst, which exhibits the smallest onset overpotential (η) of 60 mV among the above samples. The Tafel plots of different electrocatalysts are displayed in Fig. 8b, based on the linear regions of which the Tafel slope of PN-CMS40 NTs is revealed to be 98 mV dec^{-1} , smaller than that of CMS40 NTs (106 mV dec^{-1}), CoS NTs (168 mV dec^{-1}), and MoS_2 NSs (183 mV dec^{-1}). Therefore, hydrogen evolution over CMS40 NTs and PN-CMS40 NTs goes through the Volmer–Heyrovsky mechanism and the electrochemical

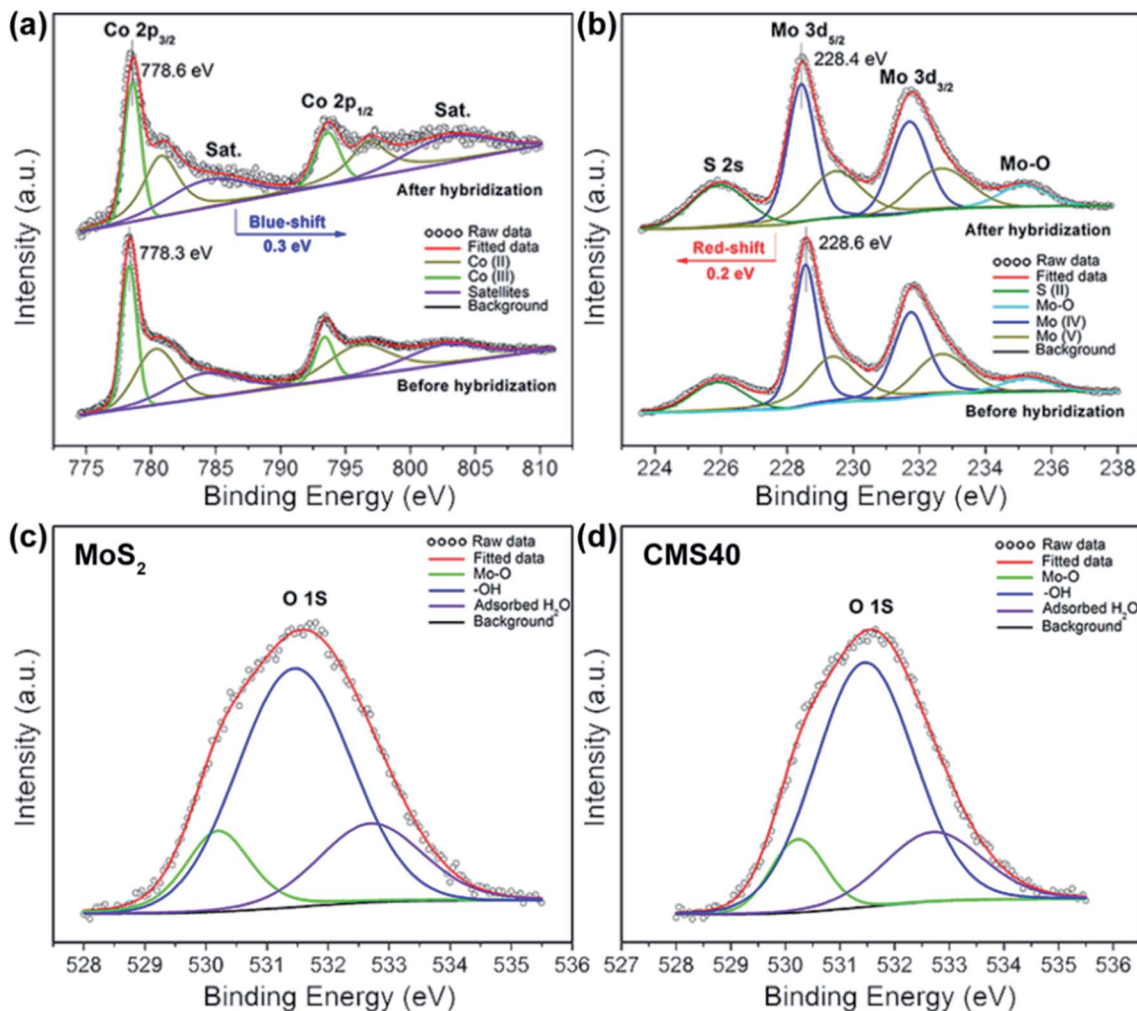


Fig. 7 (a) Co 2p and (b) Mo 3d XPS spectra of individual CoS nanotubes and MoS₂ nanosheets as well as their CoS/MoS₂ hybrid nanotubes. To verify presence of Mo–O bonds, the O 1s signals of (c) MoS₂ nanosheets and (d) CoS/MoS₂ nanotubes are displayed accordingly.

desorption process is the rate-limiting step of the HER.^{11a} In addition, by means of an extrapolation method, the exchange current densities of electrocatalysts can be obtained from the corresponding Tafel curves. As shown in Fig. S5 and Table S2,[†] the calculated exchange current density (j_0)¹⁴ of PN-CMS40 NTs is 0.21 mA cm⁻², which is much higher than 0.11 mA cm⁻² for CMS40 NTs, 0.10 mA cm⁻² for CoS NTs, and 0.085 mA cm⁻² for MoS₂ NSs. It is worth mentioning that the HER capability of PN-CMS40 NTs under alkaline conditions is superior to that of many noble-metal-free catalysts ever reported (Table S3[†]).²⁵ To get a better understanding of the electrode kinetics, electrochemical impedance spectroscopy (EIS) data of these catalysts were recorded in the galvanostatic mode. Nyquist plots presented in Fig. 8c indicate that the PN-CMS40 NTs have a smaller charge-transfer resistance^{25e} as compared to the counterparts CMS40 NTs, CoS NTs, and MoS₂ NS, which enables PN-CMS40 NTs to have a higher conductivity for facilitating the improvement of HER activity. The effective active surface areas of different electrocatalysts are positively correlated with their double layer capacitance (C_{dl}) values,^{25a,26} which can be

determined from the corresponding cyclic voltammetry (CV) curves (Fig. S10[†]) in non-faradaic potential areas (0.068–0.168 V vs. the RHE for PN-CMS40 NTs and –0.032–0.068 V vs. the RHE for CMS40 NTs, CoS NTs, and MoS₂ NSs). Based on the linear relationship between the current density and scan rate of potential (Fig. S11[†]), the C_{dl} of PN-CMS40 NTs, CMS40 NTs, CoS NTs, and MoS₂ NSs could be fixed as the slope²⁷ of 4.65, 3.63, 2.90, and 1.15 mF cm⁻², respectively. Consequently, it is rational to deduce from the C_{dl} results that more catalytically active sites can be exposed by PN-CMS40 NTs, which is responsible for their higher HER activity as compared with that of CMS40 NTs, CoS NTs, and MoS₂ NSs. For 2H-MoS₂, the unsaturated S atoms on the exposed edges of MoS₂ NSs are recognized as the active sites for the HER.²⁸ Thus, the defect-rich MoS₂ NSs prepared in this work can be provided with more additional active edge sites for enhancing their HER activity. Regarding hexagonal CoS, structurally, the Co and S atoms stack alternatively along the *c*-axis. As a result, our CoS NSs surrounded by polar {0001} facets could offer numerous low-coordination S atoms as the HER active sites. In comparison

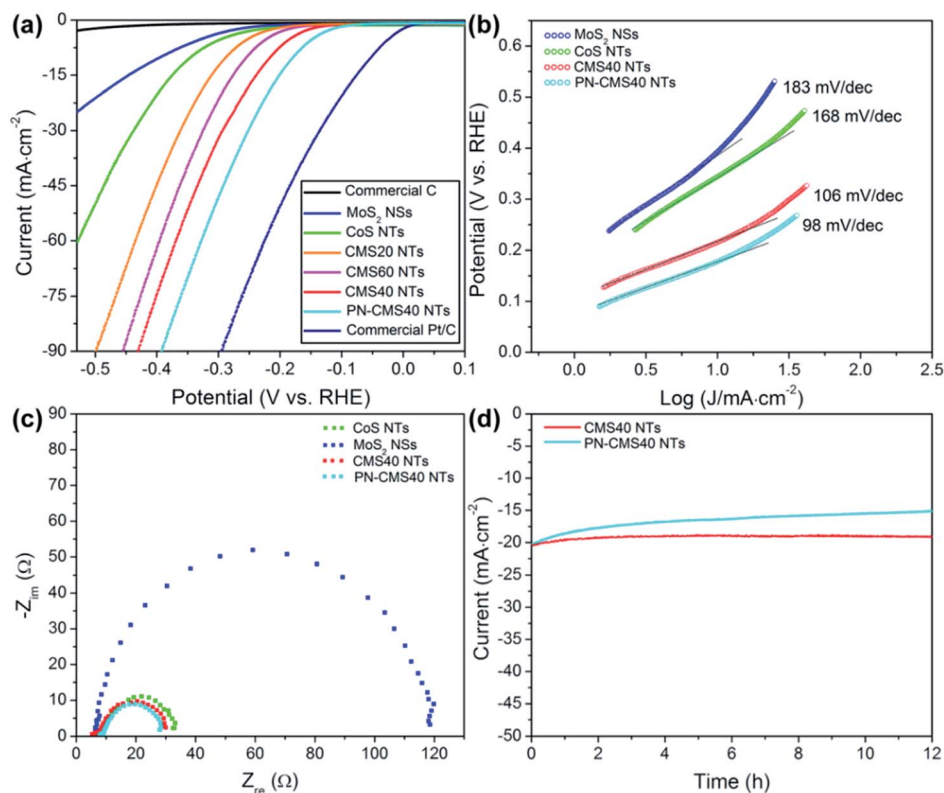


Fig. 8 (a) Polarization curves of the MoS₂ nanosheets, CoS nanotubes, Co₃S₄/MoS₂/Ni₂P nanotubes, and CoS/MoS₂ hybrid nanotubes with different composite ratios. For comparison, the data of commercial C and Pt/C (20 wt% Pt) were also given. The corresponding (b) Tafel and (c) Nyquist plots of MoS₂ nanosheets, CoS nanotubes, CoS/MoS₂ nanotubes, and Co₃S₄/MoS₂/Ni₂P nanotubes. (d) Chronoamperometric profiles of the hybrid CoS/MoS₂ nanotubes and Co₃S₄/MoS₂/Ni₂P nanotubes measured at the overpotentials of 260 and 220 mV, respectively.

with individual CoS nanosheet-assembled NTs and MoS₂ NSs, the hybrid CoS/MoS₂ NTs exhibit a much improved HER activity (Fig. 8a), which coincides well with the higher effective active surface areas and active sites of the latter as indicated by their corresponding C_{dl} values (Fig. S10 and S11[†]). The increased active sites of CoS/MoS₂ NTs could stem from the sufficient exposure of active sites by vertically grown defective MoS₂ NSs and the large number of interfaces formed between CoS NSs and MoS₂ NSs.

Furthermore, besides alkaline media, the HER performances of CMS40 NTs and PN-CMS40 NTs were also evaluated in pH = 7 phosphate buffer. As shown in Fig. S12,[†] both the CMS40 NTs and the PN-CMS40 NTs show a moderate and steady activity towards H₂ evolution in neutral solution. To examine the catalytic durability of CMS40 NTs and PN-CMS40 NTs under alkaline conditions, chronoamperometric response curves at a static overpotential were collected accordingly. It can be found from Fig. 8d that both CMS40 NTs and PN-CMS40 NTs demonstrate a negligible decay of current density for at least 12 h in 1.0 M KOH, suggesting their favourable long-term stability for the HER in alkaline solution. In addition, the morphology and composition of CMS40 NTs and PN-CMS40 NTs after 1000 potential cycling tests in the potential range of +0.2 V to −0.5 V vs. the RHE were inspected. The polarization curves in Fig. S13a and b[†] reveal that both the CMS40 NTs and

the PN-CMS40 NTs present a negligible current decay after CV cycling, agreeing well with the chronoamperometric results. We can see from the TEM images (Fig. S13c and d[†]) that the hierarchical tubular structures of CMS40 NTs and PN-CMS40 NTs were maintained after 1000 potential cycles. What's more, after cycling measurements, the XRD signals of CMS40 NTs and PN-CMS40 NTs remained nearly unchanged (Fig. S13e and f[†]), which proves clearly that the crystal phases of relevant components were well preserved during the electrocatalytic testing, indicating the eminent stability of the catalysts.

The remarkable electrocatalytic HER properties of CoS/MoS₂ NTs and Co₃S₄/MoS₂/Ni₂P NTs could be attributed to their distinctive structural advantages. Firstly, in comparison with individual MoS₂ NSs and CoS NTs, the CMS NTs exhibit a notably increased surface area (Fig. S4 and Table S1[†]). Specifically, the BET specific surface areas of MoS₂ NSs and CoS NTs are 39.6 and 45.8 m² g^{−1}, respectively, which are dramatically increased to 106 m² g^{−1} for CMS20 NTs, 112 m² g^{−1} for CMS40 NTs, and 130 m² g^{−1} for CMS60 NTs after MoS₂ NSs were grown on CoS NTs to form hybrid NTs. The higher surface areas of CoS/MoS₂ NTs will markedly facilitate the catalytic reactions by offering more active sites (Fig. S10 and S11[†]). Secondly, the open hollow structure of NTs is conducive to fast reaction kinetics by promoting the diffusion and penetration processes of reactants.²⁹ Thirdly, the interaction between the different

components of hybrid NTs (Fig. 7) could accelerate the electron transfer and give rise to positively synergistic effect, further heightening the relational catalytic activities. It should be noted that the Ni₂P-based electrocatalysts possess outstanding activities for the HER.³⁰ Due to the similarities of electronic structures between Ni₂P and hydrogenase or metal complex catalysts,³¹ the Ni₂P adopts an analogous electrocatalytic HER mechanism to the latter two.³² Hydrogenase employs pendant bases near the metal centers as the active sites for H₂ evolution,³³ while the metal complex incorporates protons transfer from pendant acid–base groups proximate to the metal center to produce H₂.³⁴ For Ni₂P of Co₃S₄/MoS₂/Ni₂P NTs, the XPS analyses (Fig. S9†) indicate that the Ni and P were provided with a small positive charge (δ^+) and a small negative charge (δ^-), respectively. Hence, in the HER with Ni₂P, the nickel centers (δ^+) and the pendant base P species (δ^-) can serve as the hydride acceptor (electron collector) and proton acceptor (proton collector), respectively, to facilitate the H₂ evolution processes efficiently.

In addition, the incorporation of oxygen into MoS₂ NSs (Fig. 1b and 7) is favorable for reducing the energy barrier of H₂ formation and enhancing the electrical conductivity,¹⁴ which contribute additionally to the improvement of HER activity. Moreover, there are abundant defects involving Mo⁵⁺ and S₂²⁻ species existing in the MoS₂ component of CMS40 NTs (Fig. 7b and S8†) and Co₃S₄/MoS₂/Ni₂P NTs (Fig. S9†), which can serve as the active sites for H₂ generation.²¹ Therefore, benefiting from the above structural advantages, these CoS/MoS₂ NTs and Co₃S₄/MoS₂/Ni₂P NTs are endowed with excellent activities towards the HER. The collective schematic illustration of H₂

formation from water electrolysis as catalyzed by the CoS/MoS₂ and Co₃S₄/MoS₂/Ni₂P NTs is shown in Fig. 9.

Conclusions

In conclusion, for the first time, hierarchical bi-component CoS/MoS₂ and tri-component Co₃S₄/MoS₂/Ni₂P hybrid nanotubes were prepared by a facile template-directed route. The synthesized nanotubes are active and stable towards hydrogen evolution in alkaline electrolytes. Especially, the Co₃S₄/MoS₂/Ni₂P nanotubes demonstrate a good HER performance with an onset overpotential of 60 mV, a Tafel slope of 98 mV dec⁻¹, and a high exchange current density of 0.21 mA cm⁻², which are superior to those exhibited by many non-noble-metal electrocatalysts. The outstanding electrocatalytic activity of the hybrid nanotubes could be attributed to their open hollow structure, large surface area and active site number, and the synergistic cooperation between different components. The synthesis tactics reported here can be extended to fabricate other novel hybrid nanotubes with tunable constituents for promising energy applications.

Conflicts of interest

The authors declare no competing financial interest.

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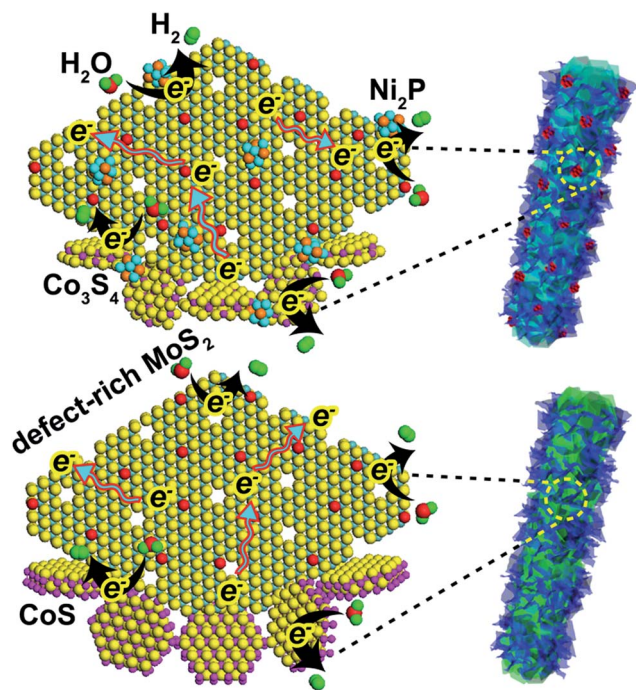


Fig. 9 A diagram illustrating the electrocatalytic H₂ evolution from H₂O splitting as induced by the bi-component CoS/MoS₂ and tri-component Co₃S₄/MoS₂/Ni₂P nanotubes.

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