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MoS$_2$ nanosheets-coated CoS$_2$ nanowire arrays on carbon cloth as three-dimensional electrodes for efficient electrocatalytic hydrogen evolution$^\dagger$

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Design and engineering of low-cost and high-efficiency electrocatalysts for hydrogen evolution reaction (HER) has attracted increasing interest in renewable energy research. Herein, MoS$_2$ nanosheets-coated CoS$_2$ nanowire arrays supported on carbon cloth (MoS$_2$/CoS$_2$/CC) were prepared by a two-step procedure that entailed hydrothermal growth of Co(OH)$_2$ nanowire arrays on carbon cloth, followed by reaction with (NH$_4$)$_2$MoS$_4$ to grow an overlayer of MoS$_2$ nanosheets. Electrochemical studies showed that the obtained 3D electrode exhibited excellent HER activity with an overpotential of $\sim$87 mV at 10 mA cm$^{-2}$, a small Tafel slope of 73.4 mV dec$^{-1}$ and prominent electrochemical durability. The results presented herein may offer a new methodology for the design and engineering of effective multilevel structured catalysts for HER based on earth-abundant components.

Introduction

Hydrogen has been hailed as a sustainable, secure, and clean alternative energy source that may satisfy the growing global energy demand. Yet such a promise will be realized only when the production of hydrogen can be carried out in an efficient, low-cost, and environmentally friendly fashion. Electrocatalytic hydrogen evolution reaction (HER) is a highly attractive means for meeting these requirements.$^{1,3}$ Among the various HER electrocatalysts, noble metals such as Pt have been the catalysts of choice thus far, but scarcity and high costs have severely limited their practical applicability.$^{5,7}$ In recent years, a great deal of research efforts have been directed to using earth-abundant and inexpensive materials to replace Pt as HER electrocatalysts, including transition metal sulfides,$^{5,11}$ selenides$^{12}$ carbides,$^{13,15}$ and phosphides.$^{16,20}$ Among these, MoS$_2$ has received particular attention due to the earth-abundant composition and high activity.$^{21-28}$ Yet, with the anisotropic structure of the sandwiched S–Mo–S layers, MoS$_2$ is prone to form a two-dimensional (2D) morphology leading to a limited number of active sites for HER.

The catalytic performance may be further improved by doping other atoms into the catalysts by manipulation of the hydrogen adsorption energy. In fact, a variety of transition metal or non-metal atoms have been used as dopants, such as Co, Ni, Li, N, Cl and O.$^{21,29-34}$ For example, the Dai group reported the synthesis of highly active and stable hybrid electrocatalysts for HER based on Co-doped iron pyrite (FeS$_2$) supported on carbon nanotubes (Fe$_{1-x}$Co$_x$S$_2$/CNT), which achieved a low overpotential of $\sim$0.12 V at 20 mA cm$^{-2}$, a Tafel slope of 46 mV dec$^{-1}$, and excellent stability over 40 h in acid solution.$^{35}$ Xie and coworkers demonstrated the synergistic regulation of both structural and electronic benefits from controllable disorder engineering and simultaneous O atoms incorporation into MoS$_2$, and observed dramatically enhanced HER activity.$^{36}$

Moreover, with increasing roughness of the electrode, one anticipates to see a decrease of the electrode size and an increase of the number of catalytic sites available for HER. Within this context, nanowires arrays integrated with a conducting substrate may enjoy the additional advantages of both charge carrier transport and the release of evolved hydrogen gas from the electrode surface.$^{36-38}$ Note that cobalt pyrite (CoS$_2$) has been reported to be catalytically active for HER with metal-like conductivity.$^{39}$ Therefore, CoS$_2$ nanowire arrays may be an ideal three-dimensional (3D) conductive substrate that features high HER activity.

In order to meet the above requirements (high electrochemical active area, high conductivity and abundant catalytic active sites), we designed and synthesized an HER electrode based on a hybrid structure consisting of CoS$_2$ nanowires coated with cobalt and oxygen co-doped MoS$_2$ nanosheets on carbon cloth (MoS$_2$/CoS$_2$/CC). The resulting nanocomposites exhibited remarkable HER stability and activity. Experimentally, CoS$_2$ nanowires arrays were used as 3D electrodes to obtain a high electrochemically active surface area. Cobalt and oxygen co-doped MoS$_2$ nanosheets were then concurrently grown on the CoS$_2$ nanowire surface. The obtained MoS$_2$/CoS$_2$ hybrids exhibited a low overpotential of only $\sim$87 mV at 10 mA cm$^{-2}$, a small Tafel slope of 73.4 mV dec$^{-1}$, and good catalytic stability.

Experimental section

Chemicals. All reagents were of analytical grade and used
without further purification. Ammonium tetrathiomolybdate ((NH₄)₂MoS₄), sodium sulfide (Na₂S), cobalt chloride (CoCl₂·6H₂O), ammonium chloride (NH₄Cl), carbamide (CO(NH₂)₂), 20 wt% Pt/C, and carbon cloth (CC) were obtained from Sinopharm Chemical Reagents Beijing Co. and used as received. Water was supplied with a Barnstead Nanopure Water System (18.3 MΩ·cm).

**Synthesis of Co(OH)₂ nanowires supported on CC.** In a typical reaction, 0.29 g of CoCl₂·6H₂O, 0.92 g of NH₄Cl, and 0.37 g of CO(NH₂)₂ were dissolved in 20 mL of Nanopure water under vigorous stirring for 30 min. Then the solution was transferred into a Teflon-lined stainless autoclave (25 mL) and a piece of CC (3.5 cm × 2.2 cm; which was cleaned by ultrasonication in acetone, ethanol and water for 20 min each prior to use). The autoclave was sealed and heated at 120 °C for 6 h in an electric oven, and then air-cooled to room temperature. The carbon cloth was taken out and washed with water thoroughly and vacuum dried. The water before being dried at 70 °C for 6 h, affording Co(OH)₂ nanowires supported on CC which were denoted as Co(OH)₂/CC.

**Synthesis of MoS₂/CoS₂ heterostructures on carbon cloth (MoS₂/CoS₂/CC).** Experimentally, 50 mg of (NH₄)₂MoS₄ was dissolved in 20 mL of Nanopure water to form a solution. Then the solution was transferred into a Teflon-lined stainless autoclave (25 mL) and a piece of Co(OH)₂/CC prepared above (2 cm × 0.5 cm) was immersed into the solution. The autoclave was heated at 200 °C for 24 h. The resulting MoS₂/CoS₂/CC (at a loading of about 18.6 mg cm⁻²) was harvested after being washed with water thoroughly and vacuum dried. CoS₂/CC (at a loading of about 16.5 mg cm⁻²) was synthesized in a similar fashion but by using 50 mg of Na₂S instead of (NH₄)₂MoS₄. Another sample, MoS₂/CC (at a loading of about 4.2 mg cm⁻²), was prepared also by the same procedure where pristine CC (2 cm × 0.5 cm) was used instead of CoS₂/CC.

**Characterizations.** Scanning electron microscopic (SEM) analysis was carried out with a FEI NOVA NanoSEM 430 field-emission microscope. Transmission electron microscopic (TEM) measurements were carried out with a JOEL JEM 2100F microscope. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Brüker D8 Advance powder X-ray diffractometer with Cu Kα (λ = 0.15406 nm) radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed using a PHI X-tool instrument (ULvac-Phi). Raman spectra were recorded on a RENISHAW inVia instrument with an Ar laser source of 488 nm in a macroscopic configuration.

**Electrochemistry.** Electrochemical measurements were performed with an electrochemical workstation (CHI 760C, CH Instruments Inc.) in a 0.5 M H₂SO₄ aqueous solution. A saturated calomel electrode (SCE, sat’d KCl) and platinum plate were used as the reference and counter electrode, respectively. The MoS₂/CoS₂/CC prepared above was used directly as a binder-free working electrode. The current densities were evaluated in terms of the geometrical surface area of MoS₂/CoS₂/CC. Polarization curves were acquired by sweeping the potential from 0 to −0.5 V (vs. RHE) at a potential sweep rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was carried out with an amplitude of 10 mV and frequency range from 100 kHz to 0.01 Hz. The main arc in each EIS spectrum was fitted using a simplified Randles equivalent circuit, which consisted of a solution resistance (Rₛ) in series with a parallel arrangement of a charge-transfer resistance (Rₜ) and a constant phase element (CPE), and the fitting parameters were estimated through the application of the Levenberg-Marquardt minimization procedure. Cyclic voltammetry (CV) was used to probe the electrochemical double layer capacitance at nonfaradaic potentials as a means to estimate the effective electrode surface area. Accelerated stability tests were performed in 0.5 M H₂SO₄ at room temperature by potential cycling between 0 and −0.4 V (vs. RHE) at a sweep rate of 100 mV s⁻¹ for a given number of cycles. Current-time responses were monitored by chronoamperometric measurements. The hydrogen gas production rate was quantified by gas chromatographic measurements (GC-2060F, LuNan Analytical Instruments, LTD, China).

**Results and discussion**

![Figure 1. SEM images of (a, b) MoS₂/CoS₂/CC, (c) CoS₂/CC and (d) MoS₂/CC. (e) XRD patterns and (f) Raman spectrum of MoS₂/CoS₂/CC. Inset to Figure 1a is an SEM image of MoS₂/CoS₂/CC at low magnification.](image-url)
entire CoS$_2$ nanowires (Figure 1b). By contrast, CoS$_2$/CC exhibited only CoS$_2$ hollow nanotubes with diameters of about 500 nm (Figure 1c), and in MoS$_2$/CC only MoS$_2$ nanosheets can be seen (Figure 1d).

Figure 1e depicts the XRD patterns of MoS$_2$/CoS$_2$/CC. One can see four sharp peaks at 20 = 32.3, 36.2, 39.8 and 55.1°, which correspond to the (200), (210), (211), and (311) planes of CoS$_2$ (JCPDS no.41-1471). The broad diffraction peaks at 20 = 26.2° arise from the CC substrate. No diffraction peak of MoS$_2$ can be detected, possibly due to a low content and a small thickness of only a few layers. However, Raman measurements (Figure 1f) of MoS$_2$/CoS$_2$/CC show two peaks at 380.2 and 405.1 cm$^{-1}$ which are characteristic for MoS$_2$, confirming the formation of MoS$_2$. Note that the peak positions are similar to those of Li-doped 1T-MoS$_2$, possibly due to Co-doping or the formation of MoS$_2$/CoS$_2$ heterostructures. In addition, the vibrational band at 981.2 cm$^{-1}$ suggested the formation of Mo-O bonds, implying the doping of O into MoS$_2$ during the decomposition of Co(OH)$_2$. The peaks at 1350.4 and 1593.8 cm$^{-1}$ are characteristic of the D and G vibrational bands of the graphitic CC substrate.

**Figure 2.** (a-c) Representative TEM images of MoS$_2$/CoS$_2$. Inset to Figure 2a is the selected area electron diffraction patterns of MoS$_2$/CoS$_2$; and inset to panel (b) is a high-resolution TEM image of MoS$_2$/CoS$_2$. (d) The corresponding EDX elemental mapping images of Mo, Co and S for MoS$_2$/CoS$_2$.

The structure and morphology of MoS$_2$/CoS$_2$ were further investigated by (HR)TEM measurements. Figure 2a shows a typical TEM image of an individual CoS$_2$ nanowire covered by thin MoS$_2$ nanosheets. The MoS$_2$ nanosheets were about 10 nm thick and grown tightly on the CoS$_2$ nanowire surface. It should be noted that the CoS$_2$ nanowires possessed a porous structure during the reaction between (NH$_4$)$_2$MoS$_4$ and Co(OH)$_2$. Thus, the interface between the CoS$_2$ backbone and the MoS$_2$ shell is difficult to identify. In the TEM image in Figure 2b, the layered structures of MoS$_2$ nanosheets can be clearly seen with an interlayer distance of 0.62 nm that is consistent with the MoS$_2$ (002) crystalline planes (inset to Figure 2b). In Figure 2c, one can see well-defined lattice fringes with a spacing of 0.27-0.28 nm, which is consistent with both CoS$_2$ (110) (0.28 nm) and MoS$_2$ (100) (0.27 nm). The coexistence of CoS$_2$ and MoS$_2$ was also manifested by the diffraction rings in the selected area electron diffraction (SAED) patterns (inset to Figure 2a).

Notably, the similar interplanar spacing between Co$_x$S$_2$ (110) and MoS$_2$ (100) suggests good lattice matching, which might be beneficial in the formation of a strong heterogeneous structure. In fact, elemental mapping studies confirmed the intimate contact between CoS$_2$ and MoS$_2$ in MoS$_2$/CoS$_2$ with a homogeneous distribution of the S element (Figure 2d). Additionally, it revealed the co-existence of Co element within MoS$_2$, in spite of the relatively low content. This suggests the formation of Co-doped MoS$_2$.

**Figure 3.** (a) XPS survey spectrum and high-resolution scans of (b) Mo 3d, (c) Co 2p and (d) S 2p electrons of MoS$_2$/CoS$_2$/CC. Black curves are experimental data and colored curves are deconvolution fits.

XPS measurements are then carried out to evaluate the chemical compositions as well as elemental valence states. The survey spectrum in Figure 3a confirms the presence of Co, Mo, S, C and O elements in MoS$_2$/CoS$_2$/CC. From the high-resolution scan in Figure 3b, the Mo 3d spectrum may be deconvoluted into two peaks at 228.3 and 231.8 eV. In addition, the characteristic peaks for Mo 3d in Mo-O and S 2p in S-O bonds can be observed at 235.3 and 168.6 eV in Figure 3b and 3d, respectively, whereas the S 2p electrons in MoS$_2$ are manifested by the two peaks at 225.8 eV and 161.7 eV. These signify O-doping in MoS$_2$. For the Co 2p electrons (Figure 3c), two distinct peaks can be identified at 780.9 and 797.6 eV, which can be assigned to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively. Furthermore, based on the integrated peak areas of Co 2p and S-O, the atomic contents of Co and O in MoS$_2$ are estimated to be 0.8 and 4.9 at%, respectively.
The iR-corrected polarization curves in Figure 4a show that the MoS$_2$ enhanced HER activity of MoS$_2$/CC is small, less than 5.2 Ω, close to that of CoS$_2$/CC (4.5 Ω), but lower than that of MoS$_2$/CC (6.3 Ω). The results confirm that CoS$_2$ possessed high conductivity due to the metal-like conductivity property. Additionally, the charge transfer resistance ($R_t$) diminished markedly with increasing overpotential from 126 Ω at ~80 mV to 4.3 Ω at ~180 mV, suggesting enhanced electron-transfer kinetics with increasing overpotentials, as depicted in Figure 4d.

In addition to excellent catalytic activity, MoS$_2$/CoS$_2$/CC also exhibited extraordinary stability in acid solution. Figure 4e depicts the polarization curves of MoS$_2$/CoS$_2$/CC before and after the stability tests of 1,000 potential cycles, where the current remained virtually unchanged. Moreover, after 25,000 s’ continuous operation at the applied potential of ~0.15 V (vs. RHE), the current density of MoS$_2$/CoS$_2$/CC remained virtually invariant, once again confirming the remarkable HER stability in 0.5 M H$_2$SO$_4$ solution (Figure 4f). In addition, one can see that the current density of the MoS$_2$/CoS$_2$/CC electrode was markedly larger than those of CoS$_2$/CC and MoS$_2$/CC at the same applied potential. The generation of hydrogen was confirmed by GC analysis (and manifested by the generation of hydrogen bubbles on the electrode surface, as depicted in Figure 4f inset), which was quantitatively consistent with those estimated from i-t data (Figure S2). The Faradaic efficiency (FE) was calculated by comparing the amount of experimentally quantified hydrogen with the theoretical value, which was 89.3% for CoS$_2$/CC, 100% for MoS$_2$/CC, and 96.8% for MoS$_2$/CoS$_2$/CC. This suggests that MoS$_2$ can improve the catalytic stability of CoS$_2$. After i-t testing, the morphologies of MoS$_2$/CoS$_2$/CC displayed no apparent changes, which confirmed the strong structural stability of the hybrid electrodes (Figure S3).

It should be noted that such an HER performance of MoS$_2$/CoS$_2$/CC (~87 mV vs. RHE at 10 mA cm$^{-2}$, Tafel slope of 73.4 mV dec$^{-1}$, and excellent catalytic stability) is better than or at least comparable to those of the MoS$_2$ or CoS$_2$-based HER electrocatalysts in acidic solution (Table S1), for instance, metallic CoS$_2$ nanosstructures (~148 mV vs. RHE at 10 mA cm$^{-2}$, and Tafel slope of 51.6 mV dec$^{-1}$), metallic CoS$_2$ nanoparamyrid arrays (~67 mV vs. RHE at 10 mA cm$^{-2}$, and Tafel slope of 70.1 mV dec$^{-1}$), Li-doped MoS$_2$/CC (~118 mV vs. RHE at 10 mA cm$^{-2}$, iR-corrected, and Tafel slope of 62 mV dec$^{-1}$), N-doped carbon-coated cobalt nanorods on a Titanium mesh (~106 mV vs. RHE at 10 mA cm$^{-2}$, and Tafel slope of 78.2 mV dec$^{-1}$).

The remarkable HER performance of the MoS$_2$/CoS$_2$ hierarchical arrays observed above might be rationalized as follows: (1) the high conductivity of the CC substrate and the metal-like CoS$_2$ facilitated electron transport during hydrogen evolution; (2) the 3D hierarchical structure of the MoS$_2$/CoS$_2$ arrays exhibited a high electrochemically active surface area with abundant active sites (double-layer capacitance 7.04 mF cm$^{-2}$, Figure S4); (3) doping by Co and O into MoS$_2$ produced abundant defect sites that served as catalytically active sites for HER, as suggested by Raman and HRTEM measurements (Figure 1f and Figure 2); and (4) the electron-transfer kinetics between CoS$_2$ and MoS$_2$ at the interface led to enhanced
electrocatalytic activity.\textsuperscript{46}

Conclusions
In this study, a nanocomposite based on MoS\textsubscript{2} nanosheets-coated CoS\textsubscript{2} nanowires arrays supported on carbon cloth (MoS\textsubscript{2}/CoS\textsubscript{2}/CC) were prepared by a two-step procedure that entailed hydrothermal growth of a Co(OH)\textsubscript{2} nanowire array on carbon cloth, followed by reaction with (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} to obtain the MoS\textsubscript{2}/CoS\textsubscript{2} composite structure. Electrochemical studies showed that the obtained 3D electrode exhibited excellent HER activity with an overpotential of \(-87\) mV at 10 mA cm\textsuperscript{-2}, a small Tafel slope of \(73.4\) mV dec\textsuperscript{-1} and prominent electrochemical durability. The high HER performance was mainly attributed to the synergistic effects of co-doping of Co and O into MoS\textsubscript{2}, and the formation of structural defects, good conductivity of metallic CoS\textsubscript{2}, and high electrochemically active surface area of the hierarchical 3D structure. The results presented herein may offer a new methodology for the design and engineering of effective HER catalysts based on earth-abundant and inexpensive components.

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MoS$_2$ nanosheets-coated CoS$_2$ nanowires arrays supported on carbon cloth exhibited excellent HER activity with an overpotential of $-87$ mV (vs RHE) at 10 mA cm$^{-2}$ due to the synergistic interactions between MoS$_2$ and CoS$_2$. 