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Dual surfactants applied in synthesis of MoSe₂ for high-efficiency hydrogen evolution reaction

Changdian Li^{a,b}, Lili Zhu^{b,c}, Han Li^{b,c}, Hui Li^{b,c}, Ziqiang Wu^{b,c}, Changhao Liang^b, Xuebin Zhu^{b,*}, Yuping Sun^{b,d,e}

^a Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, People's Republic of China

^b Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

^c University of Science and Technology of China, Hefei 230026, People's Republic of China

^d High Magnetic Field Laboratory, HFIPS, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

^e Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

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ABSTRACT

Molybdenum diselenide (MoSe₂) has been considered as a promising electrocatalyst for the hydrogen evolution reaction (HER), having great significance in the exploration of catalysts for green energy production. To obtain excellent electrocatalytic properties of MoSe₂, the structural design of materials has become a commonly-used strategy. Hence, the combination of hexadecyl trimethyl ammonium bromide (CTAB) and polyethylene-polypropylene glycol (F68) was employed during hydrothermal process to modify the structure of MoSe₂. Compared with using only one surfactant (CTAB or F68), MoSe₂ catalyst represents better surface activity, more active sites and enhanced catalytic activity in the presence of dual surfactants. The as-prepared MoSe₂-CTAB@F68 catalyst achieves an excellent HER activity with an overpotential of 189 mV versus the reversible hydrogen electrode (RHE) at a current density of 10 mA cm⁻² and a low Tafel slope of 62 mV dec⁻¹. Therefore, this work paves a way to prepare electrocatalysts with dual surfactants existence, which is greatly attractive for an optimizing electrocatalyst performance in a more efficient way. © 2020 Elsevier B.V. All rights reserved.

1. Introduction

Molecular hydrogen (H_2) as a type of pollution-free and highcalorific fuel has broad commercial applications [1,2]. Electrolysis of water is one of the crucial sources of hydrogen production, which can be divided into two heterogeneous reactions: hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [3]. Both HER and OER require high-performance electrocatalysts to reduce the electricity consumption and achieve favorable reaction kinetics [4]. Platinum (Pt) group metals and other precious-metal-based compounds are the most efficient catalysts for HER. However, the high price and scarcity of these noble metal electrocatalysts greatly limit their large-scale practical applications [5].

In the past decade, the emerging two-dimensional transition metal dichalcogenides (2D TMDs), such as molybdenum diselenide (MoSe₂), tungsten diselenide (WSe₂), tungsten disulfide (WS₂) and molybdenum disulfide (MoS₂), have been extensively investigated owing to their earth-abundant resource, low cost and promising

* Corresponding author.

E-mail address: xbzhu@issp.ac.cn (X. Zhu).

https://doi.org/10.1016/j.jallcom.2020.158092 0925-8388/© 2020 Elsevier B.V. All rights reserved. catalytic properties [6–8]. In particular, as one of the most promising electrocatalysts, $MoSe_2$ has been regarded as an excellent HER catalyst candidate due to its low hydrogen adsorption free energy ($\Delta G_H \sim 0.05 \text{ eV}$) and fascinating intrinsic electrical conductivity [9–11]. However, it is still a challenge to improve the catalytic performance of MoSe₂, which are mainly restricted by insufficient active sites [12,13]. Therefore, many efforts have been devoted to overcoming the obstacles in order to achieve MoSe₂-based HER catalysts with high performance, among which surfactant application has been confirmed as an effective route [14–18].

Till now, several types of surfactants, including cationic type such as hexadecyl trimethyl ammonium bromide (CTAB), anionic type such as sodium dodecyl sulfate (SDS) and nonionic type such as triblock copolymer (P123) and polyvinyl pyrrolidone (PVP), have been utilized to modify the structures and morphologies so as to improve the HER properties of catalysts. Guo et al. fabricated MoS₂ nanosheets with the assistance of CTAB through a facile hydro-thermal process, which resulted in a higher specific surface area, more catalytic active sites and a superior electrical conductivity for an enhanced HER performance [19]. Xu et al. utilized SDS to synthesize MoSe₂/C composites, and the experimental results indicated

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that SDS can introduce more active sites for MoSe₂ so as to significantly boost the HER activity [20]. Wang et al. fabricated the TiC-C microsphere by hydrothermal method with the assistant of P123, the as-prepared mesoporous TiC-C microsphere catalysts displayed an onset potential of 320 mV, which was 50 mV lower than the commercial TiC catalyst [21]. Dai et al. synthesized MoSe₂ nanosheets supported by PVP, and PVP could change the morphology of MoSe₂ and efficiently hinder the agglomeration of carbon atoms in reduced graphene (RGO) sheets [22]. Based on previous studies, a single surfactant has been widely employed in synthesis process of electrocatalysts, and the HER performance of electrocatalysts has been remarkably improved. Compared to a single surfactant, the usage of dual surfactants during synthesis process has been given little attention. However, the structures and morphologies of catalysts can be tuned differently when dual surfactants were employed so as to influence the HER performance. As reported, the selective dual surfactants (AOT and CTAB) were used to prepare MoS₂/NiS electrocatalysts featuring multi-level interfaces morphologies, resulting in a significantly enhanced electrocatalytic performance [16]. Therefore, we believe that the use of two kinds of surfactants will influence the structure of MoSe₂ and thus affect the HER performance.

Herein, two different surfactants (CTAB and polyethylene-polypropylene glycol (F68)) were used during hydrothermal synthesis of MoSe₂. Compared to a single surfactant (CTAB or F68), the combination of two surfactants (CTAB and F68) can induce more active sites on the surface of MoSe₂ and thus results in a better surface activity for HER [23,24]. The as-prepared MoSe₂-CTAB@F68 catalyst presents a superior HER performance with a Tafel slope of 62 mV dec⁻¹ and an overpotential of 189 mV at a current density of 10 mA cm⁻². The results will provide an effective route to prepare high-performance HER electrocatalysts.

2. Experimental section

2.1. Materials preparation

During the synthesis process, all the reagents were of analytical grade and used without further purification. Sodium borohydride and sodium molybdate dihydrate were purchased from Sinopharm Chemical Reagent Co, selenium and hexadecyl trimethyl ammonium bromide were purchased from Shanghai Alighting Biochemical Technology Co. Polyethylene-polypropylene glycol was purchased from Shanghai McLean Biochemical Technology Co. Deionized (DI) water was made in our Lab.

2.2. Synthesis of 2H-MoSe₂, MoSe₂-CTAB, MoSe₂-F68 and MoSe -CTAB@F68

1.6450 g sodium molybdate dehydrate (Na₂MoO₄·2H₂O), 1.5492 g selenium (≥ 99.99%) and 0.2595 g sodium borohydride were dispersed in 50 mL mixed solution (DI water and ethanol with a volume ratio of 1:1) with continuous magnetic stirring. After being stirred for 30 min, 0.4175 g polyethylene-polypropylene glycol (H (OCH₂CH₂)_x(OCH₂CHC H₃)_v(OCH₂CH₂)_zOH, F68) and 0.0182 g hexadecyl trimethyl ammonium bromide (C₁₉H₄₂BrN, CTAB) (99%) were added into the above solution with continuous stirring for 30 min. Afterwards, the mixed solution was transferred into a 100 mL Teflonlined stainless autoclave and kept in an electronic oven at 200 °C for 20 h. Then, the reaction system was allowed to cool down to room temperature. The final product was washed with DI water and absolute ethanol for several times and dried at 50 °C under a vacuum oven for 12 h. For convenient comparison, the 2H-MoSe₂ was prepared by the same method as mentioned-above without CTAB and F68 surfactants, the MoSe₂-CTAB was obtained with CTAB addition, and the MoSe₂-F68 was prepared in the presence of F68. Considering that the molar ratios of CTAB and F68 may influence the HER performance, we also adjusted the molar ratios of CTAB and F68 (3:7 and 7:3) to prepare the counterparts (denoted as MoSe₂-CTAB@F68 (3:7) and MoSe₂-CTAB@F68 (7:3), respectively).

2.3. Characterization

Powder X-ray powder diffraction (XRD) were measured in the 2θ range 10–80° with a Philips X'Pert Pro Super diffractometer with Cu K_{α} radiation (λ = 1.5406 Å). The morphologies and structures of the as-prepared catalysts were characterized by Field scanning electron microscope (FE-SEM, Quanta 200 FEG) and transmission electron microscope (TEM, JEM-2010 JEOL, Japan) and high-resolution transmission electron microscope (HRTEM). Element mapping and composition analysis of the samples was studied by energy-dispersive Xray spectroscopy (EDX) attached to a TEM. Raman spectroscopy was performed using a LabRAMHR 800 UV NIR spectrometer with 532 nm laser excitation. X-ray photoelectron spectra (XPS) was tested by ESCALAB 250 Xi with a monochromatic Al K_{α} source ($h\nu$ = 1486.6 eV). A drop of water was dropped on the surface of asprepared materials, and photographs of the contact angles were measured from a CCD camera at room temperature. Brunauer-Emmett-Teller (BET) analysis was performed to measure the specific surface area by using Micromeritics ASAP 2020.

2.4. Electrochemical measurements

Catalyst powder (5 mg) was dispersed in a mixture of 1000 μ L water-isopropanol (volume ratio of 5:1) and 100 μ L of 0.5 wt% Nafion solution, and then the obtained mixture was continuously sonicated to obtain a well-proportioned ink. Then 6 μ L ink was dropped on the surface of a bare glassy carbon electrode (GCE). To understand the synergistic effect of mixed surfactants on HER performance, 2H-MoSe₂, MoSe₂-CTAB, MoSe₂-F68 and MoSe₂-CTAB@F68 were studied through a series of electrochemical tests on a CHI 660E electrochemical workstation. A carbon rod was used as the counter electrode, a Ag/AgCl electrode (3 M KCl electrolyte solution inside) as the reference electrode, and the GCE with a diameter of 3 mm as the working electrode.

The HER activity of catalysts was evaluated in N₂-saturated 0.5 M H_2SO_4 solution. Linear sweep voltammetry (LSV) curves were measured at a scan rate of 5 mV s⁻¹, and cyclic voltammetry (CV) curves were conducted at various scan rates in the potential range of 0.15–0.25 V versus RHE. Double layer capacitance (C_{dl}) values were obtained from the slopes of the linear relationship between the half capacitive current density at the middle of the potential range and the scan rates. Electrochemical impedance spectroscopy (EIS) was obtained in the frequency range from 10⁵ Hz to 10⁻² Hz with an AC amplitude of 5 mV at a potential of – 0.25 V. The potential values in LSV spectra were corrected for 90% *iR* corrected based on the solution resistance determined from the EIS. All of the potentials were referenced to a reversible hydrogen electrode (RHE).

3. Results and discussion

The schematic illustration of one-pot hydrothermal synthesis process of the three multilayered MoSe₂ samples is shown in Fig. 1. At first, for the preparation of 2H-MoSe₂ nanosheets, the precursors of molybdenum (Mo) and selenium (Se) were added to the autoclave without use of any surfactant. Besides, the identical molar amounts of CTAB and dual surfactants (CTAB and F68 with a molar ratio of 5:5) were added during synthesis process for the preparation of other two counterparts (denoted as MoSe₂-CTAB and MoSe₂-CTAB@ F68, respectively).

From the XRD results (Fig. 2a), it is shown that 2H-MoSe₂ was successfully prepared. Several diffraction peaks located at 2θ of 13.49°, 33.62°, 41.45°, 54.50°, respectively, corresponding to (002),

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Fig. 1. A typical schematic diagram of the synthesis process for 2H-MoSe₂, MoSe₂-CTAB and MoSe₂-CTAB@F68.

(102), (006), (110) planes of 2H-MoSe₂ (JCPDS No. 15-0029), can be clearly seen. From the magnified XRD patterns (Fig. 2a) and the XRD result of the MoSe₂-F68 (Fig. S1a), the interlayer spacing corresponding to (002) crystalline plane of 2H MoSe₂, MoSe₂-CTAB, MoSe₂-F68 and MoSe₂-CTAB@F68 is 0.65, 0.67, 0.71 and 0.69 nm, respectively. What worth mentioning is that different surfactants can influence the interlayer spacing of MoSe₂. CTAB, as a cationic surfactant, can enter into the MoSe₂ interlayer during hydrothermal processing, resulting in the expansion of the interlayer spacing. Meanwhile, the interlayer spacing tends to decrease due to electrostatic attraction since of the cationic characteristic of CTAB [25–27]. The combined effect will lead to the expansion of the interlayer spacing. F68 is a type of nonionic surfactant with a larger molecular weight as compared with CTAB, resulting in a larger layer spacing. When F68 and CTAB are used simultaneously, the layer spacing is dominantly controlled by the F68 surfactant, while the electrostatic effect of CTAB as mentioned above will lead to the tendency of decrease in layer spacing. As a result, the layer spacing of MoSe₂-CTAB@ F68 is larger than MoSe₂-CTAB and smaller than MoSe₂-F68. Also, the XRD results of MoSe₂-CTAB@F68 (3:7 and 7:3) were also provided as shown in Fig. S2a. It can be seen that the layer spacing of MoSe₂-CTAB@F68 (7:3, 5:5 and 3:7) is slightly enlarged with the increase of F68 content.

From scanning electron microscopy (SEM) images (Fig. 2b–e), the influence of surfactants on the morphologies of MoSe₂ is clearly demonstrated. For 2H-MoSe₂, the nanosheets assemble together to form a nanoflower structure, while the morphology changes to a microsphere with numerous ridges on the surfaces with the addition of CTAB. Obviously, the use of dual surfactants does not seem to dramatically affect the morphologies compared to MoSe₂-CTAB. However, the shape of microspheres is becoming more uniform and

regular. Apart from the change of morphologies, size distribution also varies with the usage of surfactants. It is clearly seen that the particle sizes of MoSe₂-CTAB and MoSe₂-CTAB@F68 are relatively smaller than the other counterpart (2H-MoSe₂), which can be attributed to the fact that surfactant molecules can coordinate with nanoclusters, therefore inhibiting the growth of nanoparticles [28–30]. The morphology of MoSe₂-F68 also shows the features of ridges on the surface of microsphere (Fig. S1b). The morphologies of MoSe₂-CTAB@F68 (3:7 and 7:3) are displayed in Fig. S2b-c. The morphology of MoSe₂-CTAB@F68 (3:7) has no obvious change and the surface of MoSe₂-CTAB@F68 (7:3) is smoother.

The refined microstructures were further investigated by transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM). From Fig. 3a-c, it can be observed that 2H-MoSe₂ consists of curly interlaced nanosheets, showing a flower-like morphology. Obviously, in the presence of surfactants, the other two counterparts show smaller nanoscale sizes with ultra-small MoSe₂ nanosheets evenly distributed on the surface, which is in line with the SEM results. As shown in Fig. 3d-f, the HRTEM observation intuitively shows that the *d*-spacing of MoSe₂-CTAB@F68 (0.69 nm) is larger than that of both MoSe₂-CTAB (0.67 nm) and 2H-MoSe₂ (0.65 nm), which is corresponding to the XRD results. Furthermore, it can be seen that the as-prepared MoSe₂-CTAB@F68 catalysts are few-layered structures. As we know, a structural feature of few layers can be conducive to the charge transfer during the HER process [31,32]. In addition, the TEM and HRTEM images of the MoSe₂-F68 sample are exhibited in Fig. S1c-d, it is seen that the layer spacing is 0.71 nm and small size nanosheets agglomerate together.

As shown in Fig. 3g-i, the static contact angle images of 2H-MoSe₂, MoSe₂-CTAB and MoSe₂-CTAB@F68 were measured as 49.55°,



Fig. 2. (a) XRD patterns with magnified regions. Parts b-e show SEM images of (b) 2H-MoSe2, (c) MoSe2-CTAB, (d) and (e) MoSe2-CTAB@F68.



Fig. 3. Microstructures and hydrophilic results of three types of MoSe₂ samples. (a-c) TEM images, (d-f) HRTEM images and (g-i) static contact angle images.

53.92° and 38.49°, respectively. For the two surfactants used, CTAB as a cationic surfactant has a poor hydrophilicity due to the action of hydrophobic groups, while the F68 molecule has hydrophilic groups such as hydroxyl groups, leading to an enhanced hydrophilicity [33–36]. Therefore, the as-prepared MoSe₂-CTAB exhibits a poor hydrophilic property. On the one hand, an increase in the electrode hydrophilicity can be conducive to ions transportation [37]. On the other hand, evolved H₂ bubbles can be released from the electrode surface in time, and thus the electrode surface can be exposed to the electrolyte to the maximum extent [38,39].

X-ray photoelectron spectra (XPS) measurements were carried out to investigate the changes in elemental chemical states and compositions of 2H-MoSe₂, MoSe₂-CTAB and MoSe₂-CTAB@F68. It is pointed out in Fig. 4a that the Mo 3d orbit of the bare 2H-MoSe₂ displays two peaks centered at 228.7 and 231.8 eV, which are assigned to Mo (IV) $3d_{5/2}$ and Mo (IV) $3d_{3/2}$, respectively. The Se 3d peak can be divided into $3d_{3/2}$ and $3d_{5/2}$ peaks at 54.1 and 55.1 eV as depicted in Fig. 4b, respectively [10].

Additionally, the high resolution Mo (IV) 3d and Se 3d XPS spectrum of MoSe₂-CTAB has no significant changes in the correspondence with those of 2H-MoSe₂. While it can be obviously found that the Mo 3d and Se 3d peaks of MoSe₂-CTAB@F68 both show apparent shifts of 0.6 eV to lower binding energies, demonstrating that a higher electron density around the Mo and Se sites, which is conducive to the adsorption and desorption of hydrogen on the electrode surface during the catalytic process [40,41]. Moreover, the Mo (VI) 3d_{5/2} and Mo (VI) 3d_{3/2} characteristic peaks appear in the high-resolution XPS of MoSe₂-CTAB and MoSe₂-CTAB@F68, indicating that the Mo elements also have higher valence states after the surfactants treatment.

Fig. S3 contains the energy-dispersive X-ray spectroscopy (EDX) elemental mapping images of 2H-MoSe₂, MoSe₂-CTAB and MoSe₂-

CTAB@F68, respectively, indicating that Mo (red) and Se (green) elements were uniformly distributed. The corresponding EDX spectrum of MoSe₂-CTAB@F68 illustrates that the atom ratio of Mo to Se is 1:2.87 (Fig. S3a), which suggests that Mo and Se elements are nonstoichiometric ratios, and Se elements are excessive. The calculated atom ratios of Se to Mo (MoSe₂-CTAB and 2H-MoSe₂) are 2.00 and 1.98, respectively (Fig. S3b-c). To further characterize the obtained three samples, Raman measurements were carried out and the results are shown in Fig. S4. The 2H-MoSe₂ presents two characteristic Raman peaks of 2H phase at 236 and 282 cm⁻¹, corresponding to the out-of-plane A_{1g} and in-plane E_{2g}^1 vibration modes, respectively [42]. It can be observed that the A_{1g} peaks of MoSe₂-CTAB and MoSe₂-CTAB@F68 show slight shifts to smaller wavenumbers, which is possibly resulted from the changed lattice. Furthermore, the Brunauer-Emmett-Teller (BET) surface area, pore volume and nitrogen adsorption and desorption experiments of the four samples are shown in Table S1 and Fig. S5, respectively. It can be obviously seen that MoSe₂-CTAB@F68 has a larger BET value (6.86 m²/g) than 2H- $MoSe_2$ (5.10 m²/g), $MoSe_2$ -CTAB (5.09 m²/g) and $MoSe_2$ -F68 $(4.46 \text{ m}^2/\text{g})$, indicating that it can provide more active sites on the surface and facilitate contact with electrolyte [43].

The electrochemical measurements were conducted in a threeelectrode system with N₂-saturated 0.5 M H₂SO₄ electrolyte at room temperature. The corresponding results are depicted in Fig. 5 and SI. To be specific, the measured LSV curves show that compared with the overpotentials versus RHE of 2H-MoSe₂ (240 mV), MoSe₂-CTAB (172 mV) and MoSe₂-F68 (152 mV) at a current density of 1 mA cm⁻², the overpotential of MoSe₂-CTAB@F68 at the current density of 1 mA cm⁻² decreased significantly to 112 mV versus RHE (Figs. 5a and S8a). Significantly, MoSe₂-CTAB@F68 shows more superior electrocatalytic HER properties with a lower overpotential than the other three electrodes. Besides, commercial 20 wt% Pt/C catalyst, as a



Fig. 4. (a-b) High-resolution Mo 3d and Se 3d XPS spectrum of MoSe₂-CTAB@F68.



Fig. 5. HER performance of 2H-MoSe₂, MoSe₂-CTAB, MoSe₂-CTAB@F68. (a) LSV curves with a scan rate of 5 mV s⁻¹, (b) Tafel slopes derived from the LSV curves, (c) Comparison of overpotentials at 1, 10 and 50 mA cm⁻² for these catalysts, (d) Linear fits between half-capacitance current density and scan rates for the estimation of C_{dl} , (e) EIS Nyquist plots of catalysts at – 0.25 V versus RHE. Inset: the equivalent circuit model, (f) LSV comparison of MoSe₂-CTAB@F68 before and after 2000 cycles. Inset: chronopotentiometry (CP) test at 10 mA cm⁻², exhibiting the excellent long-term stability.

benchmark, was also tested with an overpotential of 33 mV versus RHE at 10 mA cm^{-2} and a Tafel slope of 32 mV dec⁻¹.

The Tafel slope, derived from the Tafel equation, ($\eta = a + b \log j$, where η is the overpotential, a is the Tafel constant, b is the Tafel slope, and j is the current density) reflects the HER mechanism of electrocatalysts [44]. As shown in Figs. 5b and S8b, MoSe₂-CTAB@F68 shows a minimum Tafel slope (62 mV dec⁻¹), less than those of 2H-MoSe₂ (82 mV dec⁻¹), MoSe₂-CTAB (74 mV dec⁻¹) and MoSe₂-F68 (73 mV dec⁻¹). The results demonstrate that dual surfactants (CTAB and F68) result in a significant decrease in the Tafel slope and thus the as-synthesized MoSe₂-CTAB@F68 reflects a faster HER rate than the other two counterparts. Furthermore, the Tafel slope is usually used to investigate the rate-determining step of an electrochemical process [45]. According to the previous report, the HER process in acidic media is mainly divided into the following three principle steps [46]:

Volmer step:

 $H_3O^+ + e^- \rightarrow H_{ads} + H_2O$, Tafel slope $\approx 120 \text{ mV dec}^{-1}$

Heyrovsky step:

 $\mathbf{H}_{ads} + \mathbf{H}_{3}\mathbf{O}^{+} \rightarrow \mathbf{H}_{2}\mathbf{O} + \mathbf{H}_{2}$, Tafel slope $\approx 40 \text{ mV dec}^{-1}$

Tafel step:

 $H_{ads} + H_{ads} \rightarrow H_2$, Tafel slope $\approx 30 \text{ mV dec}^{-1}$

Consequently, the HER process of the as-prepared MoSe₂-CTAB@ F68 electrode should follow a Volmer-Heyrovsky mechanism and the Heyrovsky step is the rate limiting step. From Fig. 5c, the histogram intuitively shows the comparison of the corresponding overpotential values of the three electrodes at the current density of 1, 10 and 50 mA cm⁻², respectively. Furthermore, it can be significantly observed that the overpotentials of MoSe2-CTAB@F68 reach 112, 189 and 240 mV versus RHE, respectively, which indicates that the HER performance is substantially improved in comparison with the other three counterparts. Moreover, the HER performance of dual surfactants with adjusted molar ratios has also been measured (Fig. S6). MoSe₂-CTAB@F68 (3:7) and MoSe₂-CTAB@F68 (7:3) require an overpotential of 238 and 245 mV at 10 mA cm⁻², and Tafel analysis gives a slope of 75 and 76 mV dec⁻¹, respectively. These results indicate that the MoSe₂ catalyst synthesized by CTAB and F68 surfactants in a molar ratio of 5:5 possesses the best HER performance.

Effective electrochemical surface area (ECSA), as a crucial factor in evaluating the HER performance of a catalyst, reflects the quantity of active sites on the catalyst surface and is directly proportional to the double-layer capacitance (C_{dl}) [47]. Cyclic voltam-mograms (CV) tests were conducted in the potential region of 0.15-0.25 V versus RHE at scan rates of 20, 40, 60, 80, 100 mV s⁻¹ (Figs. S7a-b, S8c and S9). As shown in Figs. 5d and S8d, the C_{dl} values were obtained by slopes of the fitted lines. $MoSe_2$ -CTAB@F68 yields a higher C_{dl} value to 17 mF cm^{-2} , considerably larger than 2H-MoSe_2 (1 mF cm^{-2}), $MoSe_2$ -CTAB (6 mF cm⁻²) and $MoSe_2$ -F68 (6 mF cm⁻²). Moreover, the ECSA values were derived by the values of C_{dl} [10,48]. It can be observed that MoSe₂-CTAB@F68 displays a quite high ECSA value (485 cm²), which is significantly larger than 2H-MoSe₂ (29 cm²), $MoSe_2$ -CTAB (171 cm²) and $MoSe_2$ -F68 (171 cm²), respectively. The ECSA results indicate that MoSe₂-CTAB@F68 catalyst prepared by using mixed surfactants (CTAB and F68) during the synthesis process has more active sites [27]. The increase of active sites is confirmed from the results of C_{dl} values, and the ECSA value is proportional to the C_{dl} value. MoSe₂-F68 has the largest interlayer spacing, while the BET value is the smallest and thus the active sites are significantly reduced, which ultimately leads to an inferior HER performance. The detailed calculation process is presented in SI.

To demonstrate the intrinsic conductivity and get a further understanding on the kinetics of the electrochemical behaviors under the HER process, electrochemical impedance spectroscopy (EIS) tests

	Synthesis method
SULTACTATIL TOT TEN.	²) Morphology
eculocatalysis assisted by stillgie	Mass loading (mg cm ⁻
A COMPARISON OF VALIOUS EN	Catalysts

Cdidiysis	Mass Ioduing (IIIg CIII -)		100	Electrolyte	ரப்பு அப்பட	I alel slope (IIIV dec 7)	Kel.
MoSe ₂ -CTAB	1	1	liquid-phase exfoliation	0.5 M H ₂ SO ₄	362.5	92.9	[25]
MoS ₂ -CTAB	0.285	Nanosheets	Hydrothermal	0.5 M H ₂ SO ₄	200	55	[19]
Carbon/Ni ₁₂ P ₅ -CTAB	I	Sphere	Hydrothermal	1 M KOH	176	100	[51]
PdNN	0.0169	Interconnected porous nano architecture	simple chemical route	1 M KOH	110	I	[52]
CTAB-Mo ₂ C@C	0.68	Uniform sheets	Hydrothermal and calcination	1 M KOH	100	53	[53]
MoS ₂ -VN(CTAB)	1	Nanoplates with uniform distribution	Hydrothermal and NH ₃ annealing	$0.5 \text{ M H}_2 \text{SO}_4$	180	53	[54]
PVP-MoSe ₂ @G	0.275	Nanosheets	Hydrothermal	$0.5 \text{ M H}_2 \text{SO}_4$	200	70	[22]
WS ₂ NDs	0.0163	Bulk crystallites	Liquid-phase exfoliation	0.5 M H ₂ SO ₄	~ 100	51	[15]
CTAB-MoS ₂	0.204	Dissilient hollow spheres	Hydrothermal	0.5 M H ₂ SO ₄	300	65	[55]
MoSe ₂ -CTAB MoSe ₂ -CTAB@F68	0.38	Nanosheets	Hydrothermal	0.5 M H ₂ SO ₄	235 189	74 62	This work

Table 1

were carried out at the potential of -0.25 V versus RHE from 10^5 Hz to 10^{-2} Hz. Accordingly, Fig. 5e clearly shows the Nyquist plots of these three electrodes: the symbols and solid lines, respectively, represent the experimental data and fitting data. The three catalyst samples all show two semicircles with a small semicircle at a high frequency and a large one at low frequency, corresponding to the solution interface resistance (R_{in}) and charge transfer resistance (R_{ct}) , respectively [49]. The insert of Fig. 5e states the equivalent circuit model fitted by Z View software of these electrode materials, wherein R_s presents the resistance of the electrolyte and CPE is the constant phase element. It can be obtained from the fitting circuit that the R_{ct} values are 616, 459 and 131 Ω for 2H-MoSe₂, MoSe₂-CTAB and MoSe₂-CTAB@F68, respectively. The smaller R_{ct} is, the faster reaction of the electrode will be [50]. Obviously, the MoSe₂-CTAB@ F68 electrode has the smallest R_{ct} value among all the three tested electrodes, indicating its fastest electron transfer at the electrodeelectrolyte interface. The EIS results reveal that the addition of two surfactants during the synthesis process of MoSe₂ indeed optimizes the electrical properties and enhances the conductivity of catalysts. In addition, the EIS Nyquist plots of other molar ratios of CTAB and F68 are exhibited in Fig. S7d. From the fitting circuit results, it is obtained that the R_{ct} values are of 147 and 135 Ω for MoSe₂-CTAB@ F68 (3:7) and MoSe₂-CTAB@F68 (7:3), respectively, which suggests that a slower electron transfer during HER.

Stability is one of the crucial parameters for HER process. According to the curves shown Fig. 5f, the as-prepared MoSe₂-CTAB@ F68 catalyst was cycled consecutively for 2000 cycles, and it can be found that the negative change in current density is negligible. The insertion curve shows the chronopotentiomtery (CP) test at a current density of 10 mA cm⁻² for 12 h, the polarization curve of MoSe₂-CTAB@F68 shows subtle potential fluctuation, consistent with the result from polarized curves after 2000 cycles. As a non-ionic surfactant, F68 does not ionize in water, which may be conducive to excellent stability performance [30]. Therefore, the stability results reveal that the MoSe₂-CTAB@F68 sample shows favorable cycle stability during the HER process.

In previous works, different surfactants have been explored to assist the preparation of electrocatalysts and the corresponding references for comparison are listed in Table 1. On the basis of the previous studies, this work is devoted to studying the influence of CTAB on the HER performance of MoSe₂ catalyst. In addition, the influence of dual surfactants (F68 and CTAB) on HER properties was further explored. Surprisingly, two different surfactants used simultaneously during the preparation process can make catalyst exhibit more excellent HER performance.

Compared with MoSe₂-CTAB, the electrocatalytic HER performance of MoSe₂-CTAB@F68 prepared by mixed surfactants has been remarkably enhanced, which can be attributed to the following three aspects: 1. In the presence of mixed surfactants (CTAB and F68), the as-synthesized MoSe₂ has a higher electron density around the Mo and Se sites, which can facilitate the electron transmission during the catalytic process. 2. The surface of MoSe₂-CTAB@F68 electrode has a better hydrophilic property, which can accelerate ion transport and facilitate the release of evolved hydrogen bubbles. 3. The combined effect of dual surfactants is more conducive to expose more active sites on the surfaces of catalysts and thus improve the HER performance [56].

4. Conclusions

In this work, dual-surfactant system consisting of CTAB and F68 has been proposed to improve the HER performance of MoSe₂. The as-prepared MoSe₂-CTAB@F68 electrocatalyst reveals the best HER performance compared to the other counterpart (MoSe₂-CTAB), with an overpotential of 189 mV versus RHE at 10 mA cm⁻² and a Tafel slope of 62 mV dec⁻¹. The synergistic effect of mixed surfactants not

only facilitates the exposure of more active sites on MoSe₂ catalyst surface via morphological and structural modification, but also substantially improves the hydrophilicity of the catalysts, thus effectively promoting the HER properties of catalysts. It is believed that this work will have a far-reaching influence on the application of dual-surfactant in preparation of high-quality HER electrocatalysts.

CRediT authorship contribution statement

Changdian Li: Data Curation, Formal analysis, Methodology, Roles/ Writing - original draft. **Lili Zhu, Han Li, Hui Li and Ziqiang Wu:** Writing - review & editing, Resources, Software. **Changhao Liang and Yuping Sun:** Validation, Resources, Supervision. **Xuebin Zhu:** Conceptualization, Visualization, Supervision, Validation, Funding acquisition.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2020.158092.

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