Integrating hydrogen production with selective methanol oxidation to value-added formate over a NiS bifunctional electrocatalyst

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Abstract. The sluggish kinetics of oxygen evolution reaction (OER) severely limits the efficiency of the electrocatalytic water splitting to produce hydrogen. Therefore, an effective strategy is proposed to replace the OER with selective methanol oxidation reaction (MOR). A nickel sulfide nanosheet catalyst supported on Ni foam (NiS/NF) was prepared by a facile hydrothermal method following with sulfurization treatment. The as-obtained catalyst could be used for the co-electrolysis of methanol/water to produce hydrogen and value-added formate simultaneously. The electrocatalyst can selectively oxidize methanol to formate (1.36 V vs.RHE) and the energy consumption is significantly lower than OER. Furthermore, the integrated two-electrode electrolyzer drives 10 mA cm\(^{-2}\) at a cell voltage of 1.5 V with 96\% Faradaic efficiency for MOR.

1. Introduction
Hydrogen is largely regarded as a cost-effective clean fuel in the future economy due to its wide range of sources, high calorific value and non-toxicity. Among the many hydrogen production methods, electrocatalytic water splitting is expected to play a key role combined with renewable energy power generation technology (such as solar energy, hydro, or wind power plants) [1]. In general, electrolysis of water contains two half reactions, namely, the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). However, the sluggish kinetics of the OER due to high overpotentials cause particularly significant losses to the energy efficiency of the overall process [2]. Moreover, in the process of water splitting, O\(_2\) produced by the anode is relatively less valuable and will inevitably be mixed with the H\(_2\) produced at the cathode, which means a potentially high risk of explosion [3]. In order to solve the above-mentioned problems, in addition to developing effective OER catalyst [4-6], an effective strategy is to replace OER with a relatively mild oxidation reaction with favorable thermodynamics. Many efforts have been devoted to combine HER with other organic oxidation reactions (OORs) in recent years, including 5-hydroxymethylfurfural [7], glycerol [8], urea [9], hydrazine [10], and amine [11] ect. Noticeably, this strategy not only reduces the voltage input but also avoids the possible explosion of H\(_2\)/O\(_2\) gas mixtures.

However, most of the above-mentioned organic molecules have a complex structure and/or some toxicity, leading to an increase of costs and security risks in practical application. Methanol (CH\(_3\)OH), as a simple oxygenated hydrocarbon, is cheap, highly active, and widely available (20 million tons yearly) [12]. Therefore, methanol oxidation is a desirable substitute for OER process. However, so far,
catalysts used for methanol oxidation reaction (MOR) have been mainly limited to noble-metal-based catalysts. In particular, it is still a challenge to poison the catalyst surface by CO produced by the dissociation of methanol molecules during the electrocatalytic reaction [13-15]. Furthermore, the CO produced by complete oxidation of methanol is harmful to the environment [16]. Among the products of methanol oxidation, formic acid (HCOOH) or formate (HCOO\(^{-}\)) is a kind of important industrial intermediate or product. As a safe and environmentally friendly liquid hydrogen carrier, it has been widely used in the field of fuel cells [17, 18]. Therefore, the use of low-cost electrocatalysts to achieve low-potential and highly selective controllable electrooxidation from methanol to formic acid, especially coupled with efficient HER, will be economically appealing, but still leaves high challenges.

Herein, we report the NiS nanostructure electrocatalyst supported on Ni foam (NiS/NF) by a facile hydrothermal method following with sulfurization treatment. NiS/NF as an electrocatalyst for highly selective methanol oxidation and hydrogen evolution, can simultaneously produce hydrogen and value-added formate. Importantly, a potential of as low as 1.36 V is required for the methanol oxidation at anode to reach a geometrical catalytic current density of 10 mA cm\(^{-2}\). When the as-obtained electrode is integrated into a two-electrode alkaline electrolyzer, a current density of 10 mA cm\(^{-2}\) can be obtained at a lower voltage of 1.5 V and continuous 24 h of operation without obvious decay. Furthermore, the Faradaic efficiency of formate as the only product of MOR is close to 100%.

2. **Experimental Section**

2.1. **Chemicals and materials**

Nickel (II) nitrate hexahydrate (Ni(NO\(_{3}\))\(_{2}\)·6H\(_{2}\)O, ≥ 98.0%, Macklin), urea ((NH\(_{2}\))\(_{2}\)CO, 99.0%, Sinopharm), potassium hydroxide (KOH, ≥ 90.0%, Tansoole), methanol (CH\(_{3}\)OH, 98.0%, Macklin), sodium sulfide (Na\(_{2}\)S·9H\(_{2}\)O, ≥ 98.0%, Shanghai lingfeng), Ni foam (1.0 mm × 200 mm × 250 mm, surface density: 350 g/m\(^{3}\), aperture: 0.1 mm, porosity: 97.2%, Changde Liyuan New Materials Co., Ltd.)

2.2. **Synthesis of NiS/NF Electrode**

Prior to the synthesis, Ni foam (NF) substrate (2.0 × 2.0 cm) was degreased with sonication in acetone, ethanol and DI water stepwise for 10 min, and cleaned in 3.0 mol L\(^{-1}\) HCl for 15 min to remove the surface oxide layer. Then, the pretreated NF was rinsed with DI water thoroughly. 14 mL deionized water contains 0.1163 g Ni(NO\(_{3}\))\(_{2}\)·6H\(_{2}\)O and 0.3000 g urea was transferred into a Teflon-lined stainless-steel autoclave, and a piece of cleaned NF was placed into. Then, the autoclave was sealed and kept at 120 °C for 6 h. Next, the prepared NF with Ni(OH)\(_{2}\) was taken out from the solution and washed with DI water and ethanol for three times, which was denoted as Ni(OH)\(_{2}\)/NF. Subsequently, the as-obtained Ni(OH)\(_{2}\)/NF was immersed in 1 mol L\(^{-1}\) Na\(_{2}\)S solution for 12 h at room-temperature condition to prepare the NiS/NF. Finally, the washed electrode were dried in vacuum oven at 60 °C for 12 h.

2.3. **Material Characterization**

Scanning electron microscope (SEM) images were taken with a field-emission environmental scanning electron microscope (Zeiss Sigma 500). Transmission electron microscopy (TEM) images were acquired on a JEM-2100F microscope operated at 200 kV. X-ray diffraction (XRD) was performed on a Rigaku D/max2550V with a Cu-K\(_{\alpha}\) radiation (\(\lambda=0.15418\) nm). X-ray photoelectron spectra (XPS) measurement was conducted on K-Alpha+ XPS spectrometer system (Thermo Fisher Scientific).

2.4. **Electrochemical Measurements**

MOR and HER performances were carried out in an undivided single-chamber three-electrode cell at room temperature using a Model CHI660E electrochemical workstation (Shanghai chenhua). The prepared electrode (exposure area of 0.25 × 0.25 cm) were directly used as the working electrodes. A platinum counter electrode (1 × 1.5 cm) and an Ag/AgCl (sat. KCl) reference electrode were used for all electrochemical measurements. Linear scanning voltammetry (LSV) were recorded at a scan rate of 10 mV s\(^{-1}\). The electrolyte was 20 mL of 1 mol L\(^{-1}\) KOH solution with or without 1 mol L\(^{-1}\) methanol.
All potentials reported in this work were calculated with the reversible hydrogen electrode (RHE) as follows: \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059pH + 0.197 \). Double-layer capacitances (Cdl) were calculated by CV at a potential window of 1.07-1.17 V vs. RHE with different scan rates. Electrochemical impedance spectra (EIS) measurements were performed in a frequency range from 1000,000 to 0.1 Hz with a 5 mV amplitude. For two electrode configuration, NiS/NF electrodes were used as both the anode and cathode with 20 mL 1 mol L\(^{-1}\) KOH solution containing 1 mol L\(^{-1}\) methanol. The LSV was performed at the scan rate of 50 mV s\(^{-1}\). The stability of the co-electrolysis cell was evaluated by chronopotentiometry at a current density of 10 mA cm\(^{-2}\). The long-term electrolytic reaction of MOR was conducted by chronopotentiometry at a current density of 20 mA cm\(^{-2}\). All LSV curves in this work were not iR-corrected unless specified. If there was an iR-correction, the correction equation was: \( E_{\text{corrected}} = E_{\text{measured}} - iR \).

2.5. The Products Analysis
The generated formate at the anode was detected by high performance liquid chromatography (HPLC, Agilent 1200) equipped with one Shodex RSpak KC-G and two RSpak KC-811 columns on a UV detector and a refractive index detector, using 2 mmol L\(^{-1}\) HClO\(_4\) solution as the flowing solvent. Faradaic efficiencies (FE, \%) of MOR for formate were calculated using the following equations:

\[
\text{FE}_{\text{MOR}}(\%) = \frac{n_{\text{formate}} \times 4 \times F}{Q} \times 100\%
\]

Where, \( n_{\text{formate}} \) is the molar amount of formate produced, \( F \) is the Faraday constant (96485.33 C mol\(^{-1}\)) and \( Q \) is the passed charge (C).

3. Results and Discussion
For the fabrication of NiS/NF, nickel hydroxide on Ni foam (Ni(OH)\(_2\)/NF) was prepared first through a simple hydrothermal method. Subsequently, the Ni(OH)\(_2\)/NF was immersed in Na\(_2\)S solution (1 mol L\(^{-1}\)) for 12 h at room temperature to prepare the NiS/NF electrocatalyst due to the S\(^2\) continuously replaces the OH\(^-\). The optical images (Figure 1a) clearly showed the change in the surface color of the Ni foam (from slivery white to green, and to black), indicating new species successfully grown on Ni foam (NF). The morphologies and microstructures of the prepared NiS/NF were characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Figure 1b, NiS/NF showed three-dimensional interconnected open macropores, similar to that of pristine NF (Figure 1c). A large number of nanosheets grown directly on NF (Figure 1d-e), obviously different from the relatively smooth NF skeleton (Figure 1f). A typical TEM image of a single nanoflake was presented in Figure 1g, from which we could see clearly that the diameter of the nanoflake was 300-450 nm. Moreover, the HRTEM image of the NiS/NF was demonstrated in Figure 1h-i. Except for a small amount of lattice fringes marked in yellow in Figure 1i, the whole structure was homogeneous and there was no distinguish crystalline phase, which display NiS/NF had poor crystallinity after sulfurization treatment.

![Figure 1](image-url)
In addition, the X-ray powder diffraction (XRD) patterns of the prepared electrodes were shown in Figure 2a. Apart from the effect of NF, The characteristic peaks of the Ni(OH)$_2$/NF at $2\theta = 12.5^\circ$, $24.8^\circ$ and $33.5^\circ$ were assigned to the (001), (002) and (111) lattice planes [19]. The XRD patterns of Ni(OH)$_2$ powder samples collected by centrifugation further indicated that the nickel hydroxides were grown successfully on the surface of NF. However, the characteristic peak of NiS/NF was almost difficult to observe apart from those of NF, indicating the bulk sulfurization of the obtained Ni(OH)$_2$/NF after 12 h reaction. This result was consistent with the conclusions drawn by TEM analysis. In addition, X-ray photoelectron spectroscopy (XPS) was used to detect the surface chemistry of NiS/NF. Full XPS spectra (Figure 2b) clearly verified the existence of Ni and S in NiS/NF, which was consistent with the above analysis results. In the Ni 2p XPS spectrum of NiS/NF, The existence of the Ni 2p$_{3/2}$ peak with a binding energy of 855.8 eV confirmed the Ni(II) oxidation state [20]. The peaks at 163.6 and 162.1 eV were attributed to S 2p$_{1/2}$ and S 2p$_{3/2}$, respectively, confirming the dominant form of S was S$^{2-}$ [20]. The peak value of 168.5 eV corresponded to the SO$_4^{2-}$ species on the surface caused by exposure to the air (Figure 2d) [21, 22].

![Figure 2.](image)

**Figure 2.** (a) XRD patterns of Ni(OH)$_2$ powder, Ni(OH)$_2$ on Ni foam and NiS nanoflakes on Ni foam. (b) Full XPS spectra of NiS/NF. The inset image shows relative atomic contents of Ni and S in NiS/NF. High resolution XPS spectra of the Ni 2p (c) and S 2p (d) for NiS/NF.

The electrochemical performance of NiS/NF catalytic electrode for MOR was investigated in a three-electrode configuration in alkaline electrolyte with methanol. For comparison, Ni(OH)$_2$/NF and NF substrate were also tested. Firstly, the effect of methanol concentration in 1 mol L$^{-1}$ KOH on the anodic oxidation performance of methanol was investigated, and the methanol concentration was optimized as shown in Figure 3a. When the methanol concentration increased from 2 to 4 mol L$^{-1}$, the current density was significantly decreased and the onset potential had a positive shift. It might be caused by the low conductivity of the mixed solution. The activity of MOR reached the highest in 1 mol L$^{-1}$ KOH solution containing 1 mol L$^{-1}$ methanol. According to the iR-corrected linear sweep voltammetry (LSV) polarization curves in Figure 3b, NiS/NF required a potential of a mere 1.36 V vs. RHE to reach a current density of 10 mA cm$^{-2}$ comparing to Ni(OH)$_2$/NF and bare NF, which indicated that NiS/NF had higher catalytic activity for MOR. This proves that methanol oxidation to formate reaction is an effective strategy instead of OER. Noticeably, this has a comparative advantage in the reported transition metal-based electrocatalysts for MOR (Table 1). Figure 3c further exhibited a lower Tafel slope (25 mV dec$^{-1}$) than those of Ni(OH)$_2$/NF (34 mV dec$^{-1}$) and NF substrate (116 mV dec$^{-1}$), which demonstrated that NiS/NF was kinetically beneficial for MOR. The polarization curves of Ni(OH)$_2$/NF, NF substrate and NiS/NF for MOR and OER was conducted in 1 mol L$^{-1}$ KOH with and without 1 mol L$^{-1}$ methanol.
All electrodes showed similar onset potentials for OER in the range of 1.5-1.6 V vs. RHE. The oxidation peak between 1.3 and 1.5 V vs. RHE could be ascribed to the oxidation of Ni\(^{2+}\) to Ni\(^{3+}\) [23]. The oxidation peak of Ni(OH)\(_2\)/NF and NiS/NF was no longer observed when methanol was added, showing that the electrochemically generated Ni\(^{3+}\) cations might be the active species of methanol oxidation. In fact, Ni(II) hydroxide is first oxidized to form Ni(III) oxyhydroxide in various heterogeneous Ni-based electrocatalysts, which then realize the selective conversion of alcohols [24-26]. Noticeably, The oxidation peak of NiS/NF in the OER was higher than Ni(OH)\(_2\)/NF, which indicates a more electrochemically available Ni\(^{3+}\) ions on the NiS/NF surface. According to the electrochemical impedance spectra (EIS) and the corresponding fitting results, NiS/NF electrode showed a smaller transfer resistance than Ni(OH)\(_2\)/NF (Figure 3e). Moreover, the NiS/NF possessed a larger electrochemical surface area (ECSA) as estimated by CV curves (Figure 3f). Therefore, the catalytic activity of NiS/NF for MOR was better than that of Ni(OH)\(_2\)/NF. The long-term stability of NiS/NF for MOR was also evaluated by recording U-t curves at 10 mA cm\(^{-2}\) current density. No clear increase of the anodic potential was observed over 12 h of the MOR test (Figure 3g).

As mentioned earlier, when noble-metal-based catalysts were used for MOR, the adsorption of CO might poison the active sites and cause poor stability. In addition, the final oxidation product may be the harmful greenhouse gas CO\(_2\). Thus, we studied whether there was the appearance of adsorbed CO molecules by anodic oxidation peak of CV curves in the negative sweep. However, this feature didn’t appear using NiS/NF as the electrocatalyst in the CV curves (Figure 3h), indicating that the selective oxidation of methanol to value-added formate might not involve the formation of CO-intermediate. To qualitatively and quantitatively determine the products of MOR, a long-term electrolysis test using NiS/NF as the electrode was carried out at a current density of 20 mA cm\(^{-2}\). A single signal that could be assigned to formate was observed, and the intensity gradually increased as the amount of total charge increases by the high-performance liquid chromatography (HPLC) results. Further quantification showed that the NiS/NF electrode demonstrated an average Faradaic efficiency of about 96.1% from 20 C to 100 C (Figure i).

**Figure 3.** (a) LSV curves of MOR on NiS/NF electrode in 1 mol L\(^{-1}\) KOH with varied methanol concentrations (scan rate: 10 mV s\(^{-1}\)); (b) LSV polarization curves and (c) corresponding Tafel slopes of Ni foam, Ni(OH)\(_2\)/NF, and NiS/NF in 1 mol L\(^{-1}\) KOH with 1 mol L\(^{-1}\) methanol (scan rate, 10 mV s\(^{-1}\)); (d) Comparison for LSV polarization curves of bare Ni foam, Ni(OH)\(_2\)/NF, NiS/NF in 1 mol L\(^{-1}\) KOH with and without 1 mol L\(^{-1}\) methanol. (e) Nyquist plots of Ni(OH)\(_2\)/NF, and NiS/NF; (f) results of ECSA (Ni(OH)\(_2\)/NF: 4.3 mF cm\(^{-2}\), NiS/NF: 6.7 mF cm\(^{-2}\)); (g) twelve hour stability test of NiS/NF.
for MOR at a constant current density of 10 mA cm\(^{-2}\). (h) The CV curves of NiS/NF in 1 mol L\(^{-1}\) KOH presence and absence of 1 mol L\(^{-1}\) methanol (scan rate, 10 mV s\(^{-1}\)). (i) HPLC chromatograms of the reaction products from MOR using NiS/NF as electrocatalyst at a constant current density of 20 mA cm\(^{-2}\) in 1 mol L\(^{-1}\) KOH solution containing 1 mol L\(^{-1}\) methanol with different amounts of total charge passed. The inset image shows Faradaic efficiencies of formate production for MOR on NiS/NF under different amounts of total charge passed.

**Table 1.** Comparison of reported transition-metal based electrocatalysts for MOR.

| Electrocatalyst | Electrolyte | Potential (V vs. RHE) | Corresponding current density (mA cm\(^{-2}\)) | Product\(^{*}\) | Ref. |
|----------------|-------------|-----------------------|-----------------------------------------------|----------------|-----|
| NiCu           | 1 mol L\(^{-1}\) KOH + 1 mol L\(^{-1}\) methanol | ~1.46                | 10                                            | UN            | [27]|
| NiO            | 1 mol L\(^{-1}\) KOH + 0.5 mol L\(^{-1}\) methanol | ~1.44                | 10                                            | UN            | [28]|
| Ni\(_{3}\)C/C   | 1 mol L\(^{-1}\) KOH + 0.5 mol L\(^{-1}\) methanol | ~1.43                | 10                                            | UN            | [29]|
| Ni\(_{3}\)Co\(_{2}\)Sn\(_{2}\) NPs | 1 mol L\(^{-1}\) KOH + 1 mol L\(^{-1}\) methanol | ~1.45                | 10                                            | UN            | [30]|
| 3D porous nickel networks | 1 mol L\(^{-1}\) NaOH + 1 mol L\(^{-1}\) methanol | ~1.45                | 10                                            | UN            | [31]|
| Ni\(_{1}\)Sn NPs/CB | 0.5 mol L\(^{-1}\) KOH + 0.5 mol L\(^{-1}\) methanol | ~1.48                | 10                                            | UN            | [32]|
| Co(OH)\(_{2}\)@HOS/CP | 1 mol L\(^{-1}\) KOH + 3 mol L\(^{-1}\) methanol | 1.39                 | 10                                            | Formate       | [33]\|
| NiCo\(_{2}\) | 1 mol L\(^{-1}\) NaOH + 0.5 mol L\(^{-1}\) methanol | ~1.52                | 10                                            | UN            | [34]|
| NiFe NPs       | 1 mol L\(^{-1}\) NaOH + 1 mol L\(^{-1}\) methanol | ~1.53                | 10                                            | UN            | [35]\|
| NiS/NF         | 1 mol L\(^{-1}\) KOH + 1 mol L\(^{-1}\) methanol | 1.36                 | 10                                            | Formate       | This work |

\(^{*}\)UN —— unidentified

Besides the anodic MOR, the cathodic performance of the HER was also investigated. Indeed, NiS/NF electrode also exhibited excellent activity for the HER. Compared with NF and Ni(OH)\(_{2}\)/NF, the LSV curve of NiS/NF showed a smaller onset potential in the presence or absence of methanol (Figure 4a, b). Moreover, the polarization curves of the NiS/NF electrode was further evaluated in 1 mol L\(^{-1}\) KOH solution with and without 1 mol L\(^{-1}\) methanol, aiming to assess the possible influence of methanol on the HER performance. These two LSV curves were almost coincident at low potential (Figure 4c), indicating that the influence of methanol on HER was negligible. However, the current density after the addition of methanol decreased under high potential conditions, which might be caused by the inferior conductivity of the mixed solution.

**Figure 4.** LSV curves for Ni foam, Ni(OH)\(_{2}\)/NF and NiS/NF electrodes in 1 mol L\(^{-1}\) KOH with (a) and without (b) 1 mol L\(^{-1}\) methanol (scan rate, 10 mV s\(^{-1}\)). (c) LSV curves NiS/NF for HER at a scan rate of 10 mV s\(^{-1}\) in 1 mol L\(^{-1}\) KOH with and without 1 mol L\(^{-1}\) methanol.
The outstanding bifunctional electrocatalytic performance toward HER and MOR encourage us to construct a two-electrode alkaline electrolyzer assembled by employing NiS/NF as both cathode and anode to simultaneous produce of H₂ and formate. In 1 mol L⁻¹ KOH without methanol, NiS/NF couple required cell voltages of 1.64 V to obtain 10 mA cm⁻² toward full water splitting (Figure 5a). Surprisingly, the cell voltages to afford 10 mA cm⁻² were noticeably low at 1.50 V in 1 mol L⁻¹ KOH solution containing 1 mol L⁻¹ methanol, demonstrating that MOR instead of OER was an efficient strategy to reduce the energy consumption. As shown in Figure 5b-c, the average FE of HCOO⁻ formation during different amounts of total charge passed was as high as 96.0 % at a constant current density of 20 mA cm⁻². More importantly, no bubbles were observed at the anode during bulk electrolysis reactions, indicating no noticeable competing from water oxidation. Furthermore, the NiS/NF couple was of a long-term operational stability, as evaluated by the chronopotentiometric measurement at 10 mA cm⁻² current density (Figure 5d). The applied potential did not change significantly during continuous operation of 24 h, showing the satisfying stability of NiS/NF electrode as the bifunctional catalyst.

![Figure 5.](image)

4. Conclusion
A nickel sulfide nanosheet catalyst supported on Ni foam was prepared through a simple hydrothermal method, following with a room-temperature sulfurization treatment in Na₂S solution (1 mol L⁻¹) for 12 h. When used as a dual-function electrocatalyst to produce H₂ and oxidize methanol to formate in full electrolysis cell, the voltage applied to reach a current density of 10 mA cm⁻² is only 1.50 V, lower than the voltage toward full water splitting. This process not only avoids the H₂/O₂ mixing issue of traditional water electrolysis, but also greatly improves energy efficiency. More exciting, the efficient H₂ evolution
and conversion of methanol to formate with a high selectivity of nearly 100 % are obtained simultaneously on both cathode and anode, respectively. This work provides another pathway to design and fabricate bifunctional electrocatalyst originated from nonprecious metals for the highly efficient, energy-saving and low-cost productions of valuable H2 and formate.

References
[1] FORGIE R, BUGOSH G, NEYERLIN K C, et al. Bimetallic Ru Electro catalysts for the OER and Electrolytic Water Splitting in Acidic Media [J]. Electrochemical and Solid State Letters, 2010, 13(4): D36-D9.
[2] LI P, ZHAO R, CHEN H, et al. Recent Advances in the Development of Water Oxidation Electro catalysts at Mild pH [J]. Small, 2019, 15(13): 1805103.
[3] DOTAN H, LANDMAN A, SHEEHAN S W, et al. Decoupled hydrogen and oxygen evolution by a two-step electrochemical–chemical cycle for efficient overall water splitting [J]. Nature Energy, 2019, 4(9): 786-95.
[4] XIANG K, GUO J, XU J, et al. Surface Sulfurization of NiCo-Layered Double Hydroxide Nanosheets Enable Superior and Durable Oxygen Evolution Electro catalysis [J]. ACS Applied Energy Materials, 2018, 1(8): 4040-9.
[5] ZHANG W, WANG Y, ZHENG H, et al. Embedding Ultrafine Metal Oxide Nanoparticles in Monolayered Metal–Organic Framework Nanosheets Enables Efficient Electrocatalytic Oxygen Evolution [J]. ACS Nano, 2020, 14(2): 1971-81.
[6] KANG J, SHENG J, XIE J, et al. Tubular Cu(OH)(2) arrays decorated with nanothorny Co-Ni bimetallic carbonate hydroxide supported on Cu foam: a 3D hierarchical core-shell efficient electrocatalyst for the oxygen evolution reaction [J]. Journal of Materials Chemistry A, 2018, 6(21): 10064-73.
[7] LIU W-J, DANG L, XU Z, et al. Electrochemical Oxidation of 5-Hydroxymethylfurfural with NiFe Layered Double Hydroxide (LDH) Nanosheet Catalysts [J]. ACS Catalysis, 2018, 8(6): 5533-41.
[8] LI Y, WEI X, CHEN L, et al. Nickel-molybdenum nitride nanoplate electrocatalysts for concurrent electrolytic hydrogen and formate productions [J]. Nature Communications, 2019, 10(1): 5335.
[9] SINGH T I, RAJESHKHANNA G, SINGH S B, et al. Metal–Organic Framework-Derived Fe/Co-based Bifunctional Electrode for H2 Production through Water and Urea Electrolysis [J]. ChemSusChem, 2019, 12(21): 4810-23.
[10] TANG C, ZHANG R, LU W, et al. Energy-Saving Electrolytic Hydrogen Generation: Ni2P Nanoarray as a High-Performance Non-Noble-Metal Electro catalyst [J]. Angewandte Chemie International Edition, 2017, 56(3): 842-6.
[11] HUANG C, HUANG Y, LIU C, et al. Integrating Hydrogen Production with Aqueous Selective Semi-Dehydrogenation of Tetrahydroisoquinolines over a Ni2P Bifunctional Electrode [J]. Angewandte Chemie International Edition, 2019, 58(35): 12014-7.
[12] VERHELST S, TURNER J W G, SILEGHEM L, et al. Methanol as a fuel for internal combustion engines [J]. Progress in Energy and Combustion Science, 2019, 70(43-88).
[13] ZHANG J, LIU P, MA H, et al. Nanostructured Porous Gold for Methanol Electro-Oxidation [J]. The Journal of Physical Chemistry C, 2007, 111(28): 10382-8.
[14] ZHU H, WU Z, SU D, et al. Constructing Hierarchical Interfaces: TiO2-Supported PtFe–FeOx Nanowires for Room Temperature CO Oxidation [J]. Journal of the American Chemical Society, 2015, 137(32): 10156-9.
[15] GARG A, MILINA M, BALL M, et al. Transition-Metal Nitride Core@Noble-Metal Shell Nanoparticles as Highly CO Tolerant Catalysts [J]. Angewandte Chemie International Edition, 2017, 56(30): 8828-33.
[16] JUSYS Z, KAISER J, BEHM R J. Methanol Electrooxidation over Pt/C Fuel Cell Catalysts: Dependence of Product Yields on Catalyst Loading [J]. Langmuir, 2003, 19(17): 6759-69.
[17] ZHONG H, IGUCHI M, CHATTERJEE M, et al. Formic Acid-Based Liquid Organic Hydrogen Carrier System with Heterogeneous Catalysts [J]. Advanced Sustainable Systems, 2018, 2(2): 1700161.

[18] GRASEMANN M, LAURENCEZ G. Formic acid as a hydrogen source - recent developments and future trends [J]. Energy & Environmental Science, 2012, 5(8): 8171-81.

[19] LI M, DENG X, XIANG K, et al. Value-Added Formate Production from Selective Methanol Oxidation as Anodic Reaction to Enhance Electrochemical Hydrogen Cogeneration [J]. ChemSusChem, 2020, 13(5): 914-21.

[20] TRAN V C, SAHOO S, SHIM J-J. Room-temperature synthesis of NiS hollow spheres on nickel foam for high-performance supercapacitor electrodes [J]. Materials Letters, 2018, 210(105-8.

[21] FENG L-L, YU G, WU Y, et al. High-Index Faceted Ni3S2 Nanosheet Arrays as Highly Active and Ultrastable Electrocatalysts for Water Splitting [J]. Journal of the American Chemical Society, 2015, 137(44): 14023-6.

[22] REN J-T, YUAN Z-Y. Hierarchical Nickel Sulfide Nanosheets Directly Grown on Ni Foam: A Stable and Efficient Electrocatalyst for Water Reduction and Oxidation in Alkaline Medium [J]. ACS Sustainable Chemistry & Engineering, 2017, 5(8): 7203-10.

[23] ZHU D, GUO C, LIU J, et al. Two-dimensional metal-organic frameworks with high oxidation states for efficient electrocatalytic urea oxidation [J]. Chemical Communications, 2017, 53(79): 10906-9.

[24] CHOI S, BALAMURUGAN M, LEE K-G, et al. Mechanistic Investigation of Biomass Oxidation Using Nickel Oxide Nanoparticles in a CO2-Saturated Electrolyte for Paired Electrolysis [J]. The Journal of Physical Chemistry Letters, 2020, 11(8): 2941-8.

[25] YOU B, LIU X, JIANG N, et al. A General Strategy for Decoupled Hydrogen Production from Water Splitting by Integrating Oxidative Biomass Valorization [J]. Journal of the American Chemical Society, 2016, 138(41): 13639-46.

[26] TAITT B J, NAM D-H, CHOI K-S. A Comparative Study of Nickel, Cobalt, and Iron Oxyhydroxide Anodes for the Electrochemical Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid [J]. ACS Catalysis, 2019, 9(1): 660-70.

[27] MAO Y-H, CHEN C-Y, FU J-X, et al. Electrodeposition of nickel-copper on titanium nitride for methanol electrooxidation [J]. Surface and Coatings Technology, 2018, 350(949-53.

[28] YANG W, YANG X, JIA J, et al. Oxygen vacancies confined in ultrathin nickel oxide nanosheets for enhanced electrocatalytic methanol oxidation [J]. Applied Catalysis B: Environmental, 2019, 244(1096-102.

[29] LI J, WEI R, WANG X, et al. Selective Methanol-to-Formate Electrocatalytic Conversion on Branched Nickel Carbide [J]. Angewandte Chemie-International Edition, 2020,

[30] LI J, LUO Z, HE F, et al. Colloidal Ni–Co–Sn nanoparticles as efficient electrocatalysts for the methanol oxidation reaction [J]. Journal of Materials Chemistry A, 2018, 6(45): 22915-24.

[31] GUO X, LIANG T, ZHANG D, et al. Facile fabrication of 3D porous nickel networks for electro-oxidation of methanol and ethanol in alkaline medium [J]. Materials Chemistry and Physics, 2019, 221(390-6.

[32] LI J, LUO Z, ZUO Y, et al. NiSn bimetallic nanoparticles as stable electrocatalysts for methanol oxidation reaction [J]. Applied Catalysis B: Environmental, 2018, 234(10-8.

[33] XIANG K, WU D, DENG X, et al. Boosting H2 Generation Coupled with Selective Oxidation of Methanol into Value-Added Chemical over Cobalt Hydroxide@Hydroxysulfide Nanosheets Electrocatalysts [J]. Advanced Functional Materials, 2020, 30(10): 1909610.

[34] CUI X, GUO W, ZHOU M, et al. Promoting Effect of Co in NimCon (m + n = 4) Bimetallic Electrocatalysts for Methanol Oxidation Reaction [J]. ACS Applied Materials & Interfaces, 2015, 7(1): 493-503.

[35] CANDELARIA S L, BEDFORD N M, WOEHL T J, et al. Multi-Component Fe–Ni Hydroxide Nanocatalyst for Oxygen Evolution and Methanol Oxidation Reactions under Alkaline Conditions [J]. ACS Catalysis, 2017, 7(1): 365-79.