



CrossMark
 click for updates

Cite this: *RSC Adv.*, 2017, 7, 1376

Achieving electroreduction of CO₂ to CH₃OH with high selectivity using a pyrite–nickel sulfide nanocomposite†

Siqi Zhao, Sijie Guo, Cheng Zhu, Jin Gao, Hao Li, Hui Huang,* Yang Liu* and Zhenhui Kang*

Electrochemical reduction of carbon dioxide (CO₂) to methanol (CH₃OH) catalyzed by transition metals has been proved feasible and effective in aqueous electrolytes. In this work, we introduce a FeS₂/NiS nanocomposite electrocatalyst synthesized by traditional hydrothermal method, which selectively reduces CO₂ to CH₃OH with an unprecedented overpotential of 280 mV and a high faradaic efficiency up to 64% at the potential of −0.6 V vs. reversible hydrogen electrode (RHE). The FeS₂/NiS nanocomposite electrocatalyst exhibits a stable current density of 3.1 mA cm^{−2} over a 4 hour stability test. The high selectivity towards CO₂ electroreduction to CH₃OH may be attributed to the special ladder structure of the FeS₂/NiS nanocomposite. The active sites are located at the interface between FeS₂ and NiS which can effectively suppress the side reaction hydrogen evolution reaction and facilitate the CO₂ reduction reaction.

Received 16th November 2016
 Accepted 6th December 2016

DOI: 10.1039/c6ra26868d

www.rsc.org/advances

Introduction

Electrochemical reduction of CO₂ to carbon-containing fuels is a feasible process which is conducive to solving the serious environmental problems caused by excess CO₂ such as iceberg melting, sea level rise and coastal delta subsidence.^{1–3} However, the main defects of electroreduction CO₂ are the high overpotential required to drive the reaction, the low selectivity towards various products and the high cost of catalysts.^{4,5} The high overpotential increases the consumption of energy and makes it difficult to achieve the sustainable transformation of CO₂. As for the selectivity, in addition to the major side reaction hydrogen evolution reaction (HER), the direct electroreduction of CO₂ in aqueous solution is able to generate diversiform carbon-containing chemicals.⁵ The complex products increase the challenges towards generating target product. Transition metals are commonly proposed in CO₂ reduction reaction (CO₂RR) because of their vacant orbitals and active d electrons.⁵ Among them, Au,^{6–9} Ag,^{1,10,11} and Pd^{12,13} have been explored comprehensively, while the expensive price limits the substantial application of noble metals in industry.¹⁴ Moreover, the main product from noble metals is carbon monoxide (CO), which leads to the second pollution at the cost of CO₂ consumption.

CH₃OH, as an ideal chemical, is an important intermediate of paint, plastics, and other common products.¹⁵ Besides, CH₃OH with high energy density can be stored as liquid under ambient conditions.^{16,17} The standard potential of CO₂ electroreduction to CH₃OH is only 0.016 V (vs. RHE). However, the 6 e[−] process of CO₂ reduction to form CH₃OH over the full reaction is kinetically unfavorable. Significant efforts towards selectively converting CO₂ into CH₃OH have been made since early 1983 over semiconductor materials (p-GaP and p-GaAs) with a low current density (<1 mA cm^{−2}).¹⁸ Lately, Frese *et al.* firstly observed Teflon-supported Ru electrodes could selectively reduce CO₂ to CH₃OH with a low faradaic efficiency (FE) of 42%.¹⁹ Fe,²⁰ Ni,²¹ Cu²² and their associated complexes^{23–26} have been widely investigated in the yield of CO₂RR as their rich distribution and low cost. Among them, copper is demonstrated as the effective catalyst for the electroreduction of CO₂ to hydrocarbon and alcohols.^{27,28} Le *et al.* reported that electro-deposited cuprous oxide thin films could directly reduce CO₂ to CH₃OH with a rate of 43 μmol cm^{−2} h^{−1} and low FE of 38%.²⁹ Therefore, it is urgent to seek for a highly active, selective and effective catalyst towards electroreduction CO₂ to CH₃OH.

Herein, we fabricated a low-cost FeS₂/NiS nanocomposite by traditional hydrothermal method as an excellent electrocatalyst. FeS₂/NiS nanocomposite displays incomparable operation in its low overpotential of 280 mV and high selectivity with a CH₃OH FE up to 64% at the potential of −0.6 V (vs. RHE). The stability test of FeS₂/NiS nanocomposite was performed for 4 hours, showing a stable current density of 3.1 mA cm^{−2} at −0.6 V (vs. RHE). There is no obvious degradation of the electrocatalyst after the long-time test. The following experiments reveal the

Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 199 Ren'ai Road, Suzhou, 215123, Jiangsu, PR China. E-mail: zhkang@suda.edu.cn; yangl@suda.edu.cn; hhuang0618@suda.edu.cn

† Electronic supplementary information (ESI) available: The supplementary figures are shown. See DOI: 10.1039/c6ra26868d



insight mechanism of CO₂RR catalyzed by FeS₂/NiS nanocomposite. As a comparison, we synthesized the single FeS₂ and NiS nanocrystals and applied in CO₂RR, respectively. The FeS₂ nanocrystal shows a negative onset potential at -0.45 V (*vs.* RHE) and a maximum current density of 4.2 mA cm⁻² at -0.68 V (*vs.* RHE). The NiS nanocrystal shows a more negative onset potential at -0.5 V (*vs.* RHE) and extremely low current density of 1.0 mA cm⁻² at -0.68 V (*vs.* RHE). Therefore, it can speculate that the active sites of the catalyst towards the process locate at the interface of FeS₂ and NiS. Besides, the FeS₂/NiS nanocomposite with an average diameter of 14 nm greatly increases the specific surface areas and the number of active sites.

Experiments

1. Materials

Ferric oxide (Fe₂O₃, 99%), nickel nitrate (Ni(Ac)₂, 99%), sulfur powder (99%), 1-octanol (99%), 1-octylamine (99%), ethanol (99.5%), KHCO₃ (99.7%) and Nafion perfluorinated resin solution (5 wt%) were purchased from Sigma-Aldrich and Adamas-beta; Nafion® 212 membrane was purchased from Dupont. Deionized water (purified by a Milli-Q system) was used to prepare all solutions and to rinse samples and glassware.

2. Instruments

The crystal structure of the catalyst was measured by X-ray diffraction (XRD) using an X'Pert-ProMPD (Holand) D/max-γAX-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). The high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images were obtained using a FEI/Philips Tecnai G2 F20 TWIN transmission electron microscope. The Raman spectra were acquired with an HR 800 Raman spectroscope (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. X-ray photoelectron spectroscopy (XPS) was measured using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatised Mg Kα X-ray source (hν = 1283.3 eV). Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectroscopy were performed by Carl Zeiss Supra 55 scanning electron microscope with an acceleration voltage of 20 kV. The electro-catalysis activities were measured by a Model CHI 660C workstation (CH Instruments, Chenhua, China).

3. Synthesis of catalyst

FeS₂/NiS nanocomposite. In a typical hydrothermal method,³⁰ Fe₂O₃ and Ni(Ac)₂ were introduced as iron and nickel sources, respectively. The ratio of nickel to iron is 1 : 1. Fe₂O₃ (2.5 mmol), Ni(Ac)₂ (2.5 mmol) and sulphur (50 mmol) were dissolved in 30.0 ml 1-octylamine and 30.0 ml 1-octanol at room temperature. Then, the mixture was transferred into a 150 ml stainless steel autoclave and heated to 260 °C for 3 hours under nitrogen atmosphere. When cooled to room temperature, the black precipitate was collected by centrifugation and thoroughly washed with ethanol for several times.

FeS₂ and NiS nanocrystals. The preparation of FeS₂ nanocrystal comes from the same hydrothermal method as FeS₂/NiS nanocomposite. 0.8 g Fe₂O₃ (5 mmol) and 1.6 g sulfur powder (50 mmol) were dissolved in 30.0 ml 1-octylamine and 30.0 ml 1-octanol at room temperature. Then, the mixture was transfer into a 150 ml stainless steel autoclave. The autoclave was sealed and heated to 260 °C for 3 hours under nitrogen atmosphere. The NiS nanocrystal was synthesized with the same hydrothermal method while changed the ratio of Ni(Ac)₂ and sulfur powder to 1 : 1.5.

4. Electrochemical measurements

The electrocatalytic activity measurements were performed in a standard three-electrode system. Saturated calomel electrode (SCE) was acted as the reference electrode with a standard electrode potential of 0.242 V (*vs.* RHE) and platinum wire was acted as the counter electrode. The working electrode was the catalyst modified glassy carbon disk electrode (GCE, 3.0 mm diameter CH Instruments) and 0.5 M KHCO₃ solution saturated with CO₂ was used as electrolyte. The cyclic voltammetry and linear sweep voltammetry were performed at a range from 0.7 to -0.7 V (*vs.* RHE) by a Model CHI 660C workstation under ambient condition. All the potentials reported here were *versus* Hg/HgCl₂ and were converted to the RHE scale using the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgCl}_2} + E_{\text{Hg}^0/\text{HgCl}_2}^0 + 0.0591 \times \text{pH}_{\text{electrolyte}}$$

E_{RHE} is the converted potential *versus* RHE. $E_{\text{Hg/HgCl}_2}$ is the external potential measured against the Hg/HgCl₂ reference electrode. $E_{\text{Hg}^0/\text{HgCl}_2}^0$ is the standard potential of Hg/HgCl₂ at 25 °C (0.242 V).

5. CO₂ reduction measurements and products quantification

The CO₂ reduction measurements were performed in an airtight electrochemical H-type cell under ambient temperature. The cathode compartment was consist of working electrode and reference electrode, while the anode compartment was composed of platinum wire. Apply dots of FeS₂/NiS nanocomposite catalyst (dissolved in 0.5% Nafion) to modified carbon fiber paper electrode (0.7 cm × 0.7 cm), then connect the carbon fiber paper to the cathode electrode. Each of the compartments loaded 75.0 ml 0.5 M KHCO₃ saturated with CO₂ and 40.0 ml carbon dioxide in the headspace. There is a slice of proton exchange membrane (Nafion® 212) at the connector to separate the two compartments in case the electroreduction products diffused to the anode. The electrolytic measurements were carried out under different potentials for 1 hour, respectively. The durability test was measured in an open electrolytic cell with 0.5 M KHCO₃ solution (saturated with CO₂) for 4 hours at -0.6 V. During the measurement, carbon dioxide was bubbled into water continuously with a uniform velocity. The carbon-contained gas products (CO, CH₄, C₂H₄, and C₂H₆) and major by-product (H₂) were tested by a thermal conductivity detector (TCD) with helium as the carrier gas. The liquid phase products were qualified by a NMR (Bruker AVANCEAV III 400)



spectroscopy, in which 0.5 ml electrolyte was mixed with 0.1 ml D₂O (deuterated water) and 0.05 μl dimethyl sulfoxide (DMSO, Sigma, 99.99%) was added as an internal standard.

The calculation of faradaic efficiency:

For CH₃OH,

$$FE_{\text{CH}_3\text{OH}} = \frac{6F \times n_{\text{CH}_3\text{OH}}}{I \times t} \times 100\%$$

For H₂,

$$FE_{\text{H}_2} = \frac{2F \times n_{\text{H}_2}}{I \times t} \times 100\%$$

where F is the Faraday constant, $n_{\text{CH}_3\text{OH}}$ is the moles of produced CH₃OH, and n_{H_2} for the produced H₂.

Results and discussion

To explore the surface morphology of the FeS₂/NiS nanocomposite, the SEM measurement was carried out as shown in Fig. 1a. The acquired products are made up of uniform and even nanoparticles with an average diameter of approximately 14 nm. The small and even size of the electrocatalyst confirms high specific surface area and incremental active sites, which effectively improve the catalysis activity. The HRTEM image of FeS₂/NiS nanocomposite is shown in Fig. 1b. The characteristic lattice spacing of 0.27 nm is corresponding to the (200) plane of FeS₂ whose XRD peak is located at $2\theta = 33.0$.³⁰ The lattice spacing of 0.29 nm is indexed to the (100) plane of the NiS which matches to the XRD peak at $2\theta = 46.0$.³¹ Fig. 1c shows the

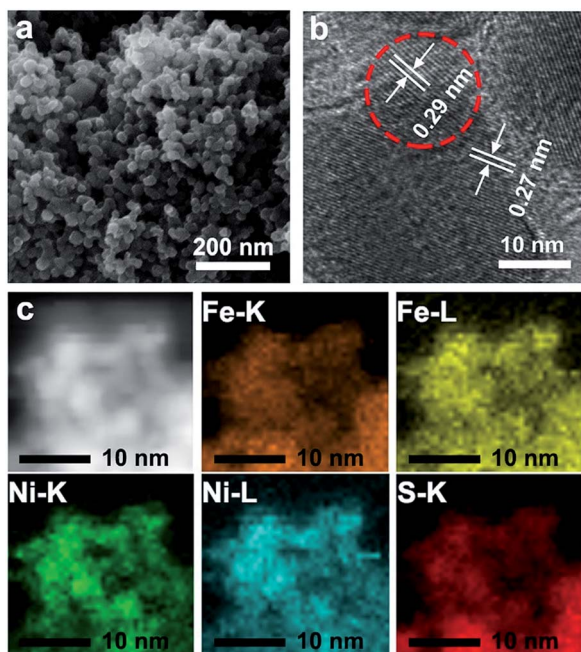


Fig. 1 (a) The SEM image of FeS₂/NiS nanocomposite. (b) The HRTEM image of FeS₂/NiS nanocomposite. (c) STEM image and corresponding chemical elements mappings of Fe-K, Fe-L, Ni-K, Ni-L and S-K of FeS₂/NiS nanocomposite.

STEM image and corresponding chemical mappings of Fe-K, Fe-L, Ni-K, Ni-L and S-K for FeS₂/NiS nanocomposite. A homogeneous distribution of Fe, Ni, and S is reviewed in the nanocomposite. Furthermore, the HRTEM image concludes that the germination of FeS₂/NiS nanocomposite arranges intimately rather than the simple physical mixture of the two compounds. Thus, we proposed that the active sites of CO₂ electroreduction locate at the interface between FeS₂ (200) and NiS (100).

In order to identify the crystallinity and structure of the FeS₂/NiS nanocomposite, the XRD measurements were performed. Fig. 2a shows the XRD patterns of FeS₂/NiS nanocomposite (brown trace), FeS₂ standard card (blue trace) and NiS standard card (red trace). The phanic peaks can be completely matched to the FeS₂ (JCPDS no. 42-1340) and NiS (JCPDS no. 02-1280) standard diffraction peaks. In details, the predominant peaks at 46.0, 53.7, 30.2 and 34.7 degree correspond to the (100), (202), (101) and (102) planes of NiS, respectively. The peaks at 33.0, 56.4, 37.1 and 47.5 degree are assigned to the (200), (311), (210) and (211) planes of FeS₂, respectively. There are no impurity peaks from other crystal structures. The average size of FeS₂/NiS nanocomposite is ~14 nm from the line width analysis of the diffraction peak calculated by Scherer equation, which is consistent with the SEM observation. FeS₂/NiS nanocomposite was further characterized with Raman spectrum and showed in Fig. 2b. The peaks at 340 and 378 cm⁻¹ can be well attributed to Raman vibrations of pyrite FeS₂ and no other impurity peaks from marcasite and troilite.³⁰ The peaks at 222 and 285 cm⁻¹ are matching with NiS completely.³² The peaks assigned to NiS at 335 and 376 cm⁻¹ are not emerged in the diagram obviously, which is resulted by the overlap with the peaks of pyrite FeS₂.

The XPS measurement was introduced to confirm the element proportion and valence state of the FeS₂/NiS nanocomposite. Besides the Fe, Ni and S elements from FeS₂/NiS nanocomposite, C and O elements are also detected in the full spectrum (as shown in Fig. 3a). The elements of C and O may attribute to the carbonization of the solvents. The high resolution spectra of C 1s and O 1s are shown in Fig. S1.† The binding energy at 284.8, 286.4 and 288.8 eV of C 1s are consistent with graphite carbon, C-OH and C=O, respectively.³³ The O 1s peaks at 531.9 and 532.9 eV from oxygen atoms are attributed to C=O and O-C, respectively.³⁴ The carbonized solvents with oxygenic functional groups may not only improve the stability of the

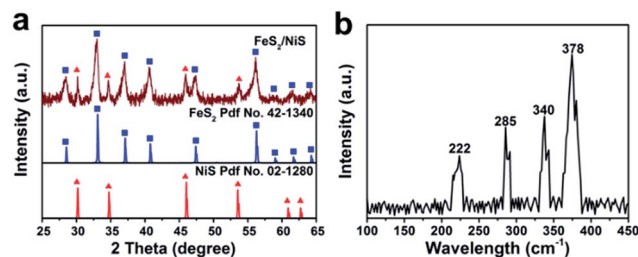


Fig. 2 (a) The large-angle XRD patterns of FeS₂/NiS nanocomposite (brown trace), FeS₂ (blue trace) and NiS (red trace). (b) Raman spectrum of FeS₂/NiS nanocomposite.



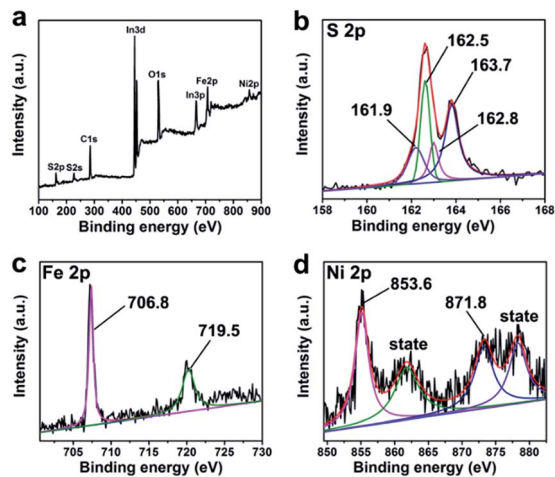


Fig. 3 (a) The full XPS spectrum of FeS₂/NiS nanocomposite and the high-resolution XPS spectra of (b) S 2p, (c) Fe 2p and (d) Ni 2p.

catalyst but also act as a support.³⁵ The high resolution scan spectra of the Fe 2p, Ni 2p and S 2p are presented in Fig. 3b–d. The atomic ratio of Fe to Ni is equal to 2 according to the XPS calculation. The result is consistent with the EDX spectroscopy measurement (as shown in Fig. S2†). The binding energy at 706.8 and 719.5 eV are conformed to the Fe 2p^{3/2} and Fe 2p^{1/2} which are characterized of pyrite.³⁶ The Ni 2p^{3/2} and Ni 2p^{1/2} peaks are observed at 853.6 and 871.8 eV, exist two satellite peaks at 858.7 and 878.1 eV respectively,³² indicating that the nickel existed in bivalent states. There are four peaks in the high resolution XPS spectra of S. The S 2p^{3/2} and S 2p^{1/2} peaks located at 161.9 and 162.8 eV are consistent with S²⁻,³¹ while the peaks at 162.5 and 163.7 eV are identified with the S 2p^{3/2} and S 2p^{1/2} of S₂²⁻.³⁷ These results indicate that both S₂²⁻ and S²⁻ are existed. Thus, we integrate the peak areas respectively and acquire the ratio of S₂²⁻ to S²⁻ is 2, which is also consistent with the previously calculated ratio of iron to nickel.

In typical experiments, the electrolytic activities were measured in a three-electrode system in 0.5 M KHCO₃ aqueous solution. The curves of Linear Sweep Voltammetry (LSV) for the FeS₂/NiS nanocomposite are shown in Fig. 3a. The black curve shows the catalytic activity for HER under N₂ atmosphere (pH = 8.5), which presents a high overpotential over 450 mV and a low current density of 2.5 mA cm⁻² with the applied potential up to -0.68 V. In comparison, an obvious enhancement of current density of 7.8 mA cm⁻² is observed at the potential of -0.68 V when the electrolyte is saturated with CO₂ (pH = 7.5). The onset potential performs more positive at -0.30 V, indicating a low overpotential less than 280 mV (confirmed by GC and ¹H NMR). The results reveal that the electrocatalyst can selectively reduce CO₂ and suppress the HER efficiently under CO₂ atmosphere.

As a comparison, we investigated the electrocatalytic performances of FeS₂ nanocrystal and NiS nanocrystal for CO₂ electroreduction, respectively. The detailed synthetic process is shown in Experiment section. The specific characterizations including XRD, SEM and TEM of the as-prepared FeS₂ and NiS nanocrystals are shown in Fig. S3 and S4.† The LSVs of FeS₂, NiS

and FeS₂/NiS were measured in CO₂-saturated 0.5 M KHCO₃ solution. As showed in Fig. 4b, both the single FeS₂ and NiS nanocrystals show poor activities towards CO₂RR compared with FeS₂/NiS nanocomposite, in which the FeS₂ shows an onset potential at -0.45 V for HER and the maximum current density of 4.2 mA cm⁻² at -0.68 V. While the NiS nanocrystal performs even worse, which shows an extremely low current density of 1 mA cm⁻² at -0.68 V (red trace). It is generally known that FeS₂ is feasible towards HER.^{38,39} For FeS₂/NiS nanocomposite (black trace), more positive onset potential at -0.3 V as well as higher current density of 7.8 mA cm⁻² can be achieved towards CO₂RR.

To further compare the electrocatalytic performance of FeS₂ nanocrystal, NiS nanocrystal and FeS₂/NiS nanocomposite for CO₂ reduction, the electrolytic reduction reaction of CO₂ was carried out in an electrochemical airtight H-type cell at the potential range from -0.3 to -0.7 V. The gas products were detected by gas chromatography (GC). The liquid-phase products were detected by ¹H NMR and the DMSO was added as an internal standard. As shown in Fig. S5,† the reduced products are CH₃OH after CO₂ electroreduction catalyzed by FeS₂/NiS nanocomposite for 2 hours and 4 hours. For FeS₂ and NiS nanocrystals, H₂ is the only product in gas phase and no hydrocarbon products are detected in both gas and liquid phases. As shown in Fig. 4c, the FEs vs. the applied potentials (-0.5, -0.6, -0.7 V) of H₂ for FeS₂ and NiS nanocrystals show a stable tendency at different potentials. For FeS₂/NiS nanocomposite, the FEs vs. the applied potentials (-0.3, -0.4, -0.5, -0.6, -0.7 V) for CH₃OH (left axis) and H₂ (right axis) are shown in Fig. 4d. The CH₃OH FEs show an overall growth tendency at the range from -0.3 V to -0.6 V but reach a plateau of 64% approximately at -0.6 V. After that, it maintains a stable tendency. We further compared the FEs for CH₃OH in the literatures and showed in Table S1.† To reach the same FE of

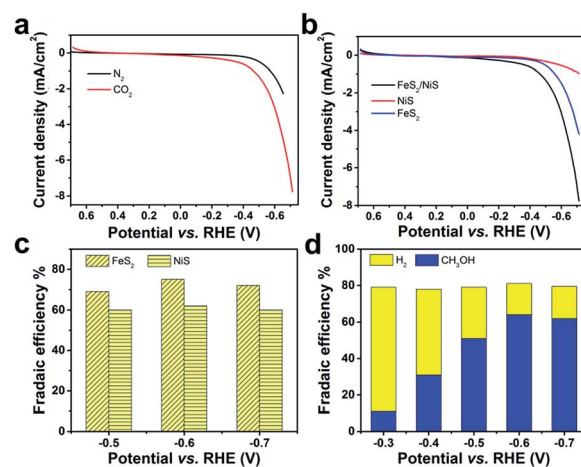


Fig. 4 (a) LSVs of FeS₂/NiS nanocomposite in 0.5 M KHCO₃ aqueous solution under N₂ (blue trace) and CO₂ (red trace) atmosphere; (b) LSVs of FeS₂/NiS nanocomposite (black trace), NiS (red trace), and FeS₂ (blue trace) in 0.5 M KHCO₃ aqueous solution under CO₂ atmosphere; (c) faradaic efficiencies vs. potential of H₂ for FeS₂ and NiS nanocrystals; (d) faradaic efficiencies vs. potential of CH₃OH and H₂ for FeS₂/NiS nanocomposite.



CH₃OH, FeS₂/NiS nanocomposite shows a moderate potential compared with those noble metal electrocatalysts. The H₂ FEs for FeS₂/NiS nanocomposite show an opposite tendency compared with CH₃OH. The FEs of H₂ continuously decreases and decreases to a minimum of 17% at the applied potential of -0.6 V. Moreover, the total FEs for the generation of CH₃OH and H₂ are maintained at 81% over the whole process. These results demonstrate that single FeS₂ and NiS nanocrystals can hardly reduce CO₂ into hydrocarbon products, whereas the FeS₂/NiS nanocomposite can achieve an efficient and selective electroreduction process for CO₂. Thus, we propose the active sites for CO₂RR locate at the interface between FeS₂ and NiS.

To further prove the stability of the FeS₂/NiS nanocomposite, the continuous tendency test was measured in a standard three-electrode cell as shown in Fig. 5a. A stable current density of 3.1 mA cm⁻² is observed over the 4 hours electroreduction at the potential of -0.6 V. Besides, the FE of the products (CH₃OH and H₂) for the FeS₂/NiS nanocomposite is maintained at about 81% over the 4 hours electrolysis. It can observe no obvious deactivation of FeS₂/NiS nanocomposite for CO₂ reduction throughout the entire process. Then, the XRD measurement was performed on the reacted FeS₂/NiS nanocomposite as shown in Fig. 5b. The XRD analysis indicates that there is no transformation taking place upon the catalyst during the whole electroreduction. These results fully confirm that FeS₂/NiS nanocomposite is excellently stable and efficient for CO₂ electroreduction.

To understand the highly efficient electrocatalysis activity of FeS₂/NiS nanocomposite, we further compared the performances of CO₂RR catalysed by FeS₂/NiS nanocomposite, pure FeS₂ and NiS nanocrystals. The single FeS₂ and NiS nanocrystals show poor activities towards CO₂RR. The FeS₂ nanocrystal shows a negative onset potential at -0.45 V and the maximum current density of 4.2 mA cm⁻² at -0.68 V. Then, the NiS nanocrystal shows a more negative onset potential at -0.5 V and extremely low current density of 1 mA cm⁻² at -0.68 V. Furthermore, a physical mixture of FeS₂ and NiS nanocrystals with the same ratio as FeS₂/NiS nanocomposite was fabricated. The electrocatalytic activity for CO₂ reduction was measured and showed in Fig. S6.† The current density presents a slight increase under CO₂ atmosphere compared with N₂ atmosphere. Then, a 2 h-electrolysis in 0.5 M CO₂-saturated KHCO₃ for the physical

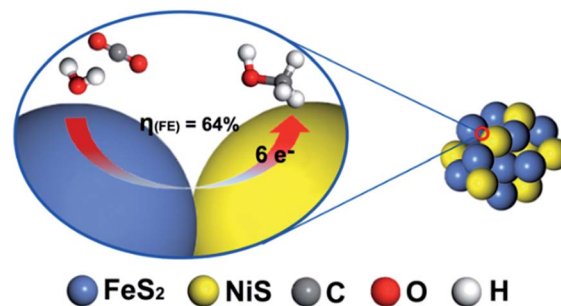


Fig. 6 The proposed reaction mechanism of electroreduction CO₂ by FeS₂/NiS nanocomposite electrocatalyst.

mixture was performed at the potential of -0.6 V. Only H₂ was detected in the both gas phase and liquid phase products. The increase of current density may be ascribed to the effect of pH. In contrast, the FeS₂/NiS nanocomposite exhibits excellent activity for CO₂RR. It achieves an unprecedented overpotential of 280 mV and a stable current density of 3.1 mA cm⁻² at the potential of -0.6 V. Comparing the electrocatalytic performances of CO₂RR in FeS₂ nanocrystal, NiS nanocrystal, physical mixture of FeS₂ and NiS nanocrystals and FeS₂/NiS nanocomposite, it can speculate that the active sites of the catalyst locate at the interface between FeS₂ (200) and NiS (100) (as shown in Fig. 6). On the other hand, many researches have evidenced that the electroreduction of CO₂ to CH₃OH is a complex process which includes the transformation of 6 e⁻ and 6 H⁺.^{5,37-40} Still, more experimental and theoretical calculations are needed to unravel the detailed mechanism of this multistep reaction.

Conclusion

We synthesized the FeS₂/NiS nanocomposite with a traditional hydrothermal method. It was demonstrated that FeS₂/NiS nanocomposite can catalyze CO₂RR at an unprecedented overpotential of 280 mV and a high CH₃OH faradaic efficiency up to 64% at the potential of -0.6 V. Moreover, the catalyst performs a stable current density of 3.1 mA cm⁻² over the 4 hours stability test and there is no obvious degradation after electroreduction from XRD observation. In experiments, the FeS₂ nanocrystals, NiS nanocrystals and the physical mixture of FeS₂ and NiS nanocrystals all show poor activity towards CO₂RR, while the FeS₂/NiS nanocomposite exhibits excellent activity towards the process. Thus, the high activity and selectivity towards CO₂ electroreduction to CH₃OH is probably attributed to the special ladder structure of the FeS₂/NiS nanocomposite. The active sites may locate at the interface between FeS₂ and NiS which could effectively suppress the side reaction of HER and facilitate the CO₂RR. The low-cost FeS₂/NiS nanocomposite is an efficient alternative to expensive materials for the application of CO₂ electroreduction in industry.

Acknowledgements

This work is supported by the Collaborative Innovation Center of Suzhou Nano Science and Technology, the National Natural

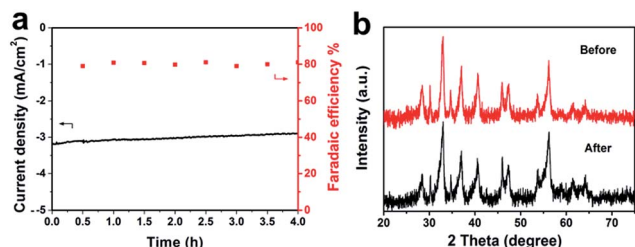


Fig. 5 (a) Stability of FeS₂/NiS nanocomposite for CO₂ reduction operated at a potential of -0.6 V vs. RHE for 4 hours. Geometric current density vs. time (left axis) and total FE for production (CH₃OH and H₂) vs. time (right axis); (b) the large-angle XRD patterns of FeS₂/NiS nanocomposite before (red trace) and after (black trace) 4 hours electroreduction.



Science Foundation of China (51422207, 51132006, 51572179, 21471106, 21501126), the Specialized Research Fund for the Doctoral Program of Higher Education (20123201110018), a Suzhou Planning Project of Science and Technology (ZXG2012028), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Notes and references

- Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen and F. Jiao, *Nat. Commun.*, 2014, **5**, 3242.
- R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya and P. Strasser, *J. Am. Chem. Soc.*, 2014, **136**, 6978–6986.
- J. Wu, R. M. Yadav, M. Liu, P. P. Sharma, C. S. Tiwary, L. Ma, X. Zou, X.-D. Zhou, B. I. Yakobson, J. Lou and P. M. Ajayan, *ACS Nano*, 2015, **9**, 5364–5371.
- J. O. Bockris, *J. Electrochem. Soc.*, 1989, **136**, 2521.
- J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631–675.
- W. Zhu, R. Michalsky, Ö. Metin, H. Lv, S. Guo, C. J. Wright, X. Sun, A. A. Peterson and S. Sun, *J. Am. Chem. Soc.*, 2013, **135**, 16833–16836.
- S. Back, M. S. Yeom and Y. Jung, *ACS Catal.*, 2015, **5**, 5089–5096.
- H. Mistry, R. Reske, Z. Zeng, Z.-J. Zhao, J. Greeley, P. Strasser and B. R. Cuenya, *J. Am. Chem. Soc.*, 2014, **136**, 16473–16476.
- W. Zhu, Y.-J. Zhang, H. Zhang, H. Lv, Q. Li, R. Michalsky, A. A. Peterson and S. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 16132–16135.
- J. Rosen, G. S. Hutchings, Q. Lu, S. Rivera, Y. Zhou, D. G. Vlachos and F. Jiao, *ACS Catal.*, 2015, **5**, 4293–4299.
- S. Ma, R. Luo, J. I. Gold, A. Z. Yu, B. Kim and P. J. A. Kenis, *J. Mater. Chem. A*, 2016, **4**, 8573–8578.
- D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang and X. Bao, *J. Am. Chem. Soc.*, 2015, **137**, 4288–4291.
- X. Wang, H. Shi, J. H. Kwak and J. Szanyi, *ACS Catal.*, 2015, **5**, 6337–6349.
- Y. Gong, Y. Zhao, Y. Chen, Y. Wang and C. Sun, *RSC Adv.*, 2016, **6**, 43185–43190.
- J. Albo, M. Alvarez-Guerra, P. Castaño and A. Irabien, *Green Chem.*, 2015, **17**, 2304–2324.
- C. Zhai, M. Zhu, F. Pang, D. Bin, C. Lu, M. C. Goh, P. Yang and Y. Du, *ACS Appl. Mater. Interfaces*, 2016, **8**, 5972–5980.
- C. Zhai, M. Zhu, D. Bin, F. Ren, C. Wang, P. Yang and Y. Du, *J. Power Sources*, 2015, **275**, 483–488.
- D. Canfield and K. W. Frese, *J. Electrochem. Soc.*, 1983, **130**, 1772.
- K. W. Frese and S. Leach, *J. Electrochem. Soc.*, 1985, **132**, 259–260.
- K. Hara, A. Kudo and T. Sakata, *J. Electroanal. Chem.*, 1995, **386**, 257–260.
- A. Kudo, S. Nakagawa, A. Tsuneto and T. Sakata, *J. Electrochem. Soc.*, 1993, **140**, 1541–1545.
- K. Hara, A. Tsuneto, A. Kudo and T. Sakata, *J. Electrochem. Soc.*, 1994, **141**, 2097–2103.
- S. Bagherzadeh and N. P. Mankad, *J. Am. Chem. Soc.*, 2015, **137**, 10898–10901.
- G. Kyriacou and A. Anagnostopoulos, *J. Electroanal. Chem.*, 1992, **322**, 233–246.
- J. B. Varley, H. A. Hansen, N. L. Ammitzbøll, L. C. Grabow, A. A. Peterson, J. Rossmeisl and J. K. Nørskov, *ACS Catal.*, 2013, **3**, 2640–2643.
- A. B. Bocarsly, Q. D. Gibson, A. J. Morris, R. P. L'Esperance, Z. M. Detweiler, P. S. Lakkaraju, E. L. Zeitler and T. W. Shaw, *ACS Catal.*, 2012, **2**, 1684–1692.
- H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser and B. R. Cuenya, *Nat. Commun.*, 2016, **7**, 12123.
- D. Raciti, K. J. Livi and C. Wang, *Nano Lett.*, 2015, **15**, 6829–6835.
- M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz and J. C. Flake, *J. Electrochem. Soc.*, 2011, **158**, E45.
- B.-B. Yu, X. Zhang, Y. Jiang, J. Liu, L. Gu, J.-S. Hu and L.-J. Wan, *J. Am. Chem. Soc.*, 2015, **137**, 2211–2214.
- J. Yuan, J. Wen, Y. Zhong, X. Li, Y. Fang, S. Zhang and W. Liu, *J. Mater. Chem. A*, 2015, **3**, 18244–18255.
- J. S. Chen, J. Ren, M. Shalom, T. Fellingner and M. Antonietti, *ACS Appl. Mater. Interfaces*, 2016, **8**, 5509–5516.
- L. Bai, S. Qiao, Y. Fang, J. Tian, J. Mcleod, Y. Song, H. Huang, Y. Liu and Z. Kang, *J. Mater. Chem. C*, 2016, **4**, 8490–8495.
- B. Y. Yu and S.-Y. Kwak, *J. Mater. Chem.*, 2012, **22**, 8345.
- H. Li, X. Zhang and D. R. MacFarlane, *Adv. Energy Mater.*, 2015, **5**, 1401077.
- F. Jiang, L. T. Peckler and A. J. Muscat, *Cryst. Growth Des.*, 2015, **15**, 3565–3572.
- R. Morrish, R. Silverstein and C. A. Wolden, *J. Am. Chem. Soc.*, 2012, **134**, 17854–17857.
- D.-Y. Wang, M. Gong, H.-L. Chou, C.-J. Pan, H.-A. Chen, Y. Wu, M.-C. Lin, M. Guan, J. Yang, C.-W. Chen, Y.-L. Wang, B.-J. Hwang, C.-C. Chen and H. Dai, *J. Am. Chem. Soc.*, 2015, **137**, 1587–1592.
- D. Jasion, J. M. Barforoush, Q. Qiao, Y. Zhu, S. Ren and K. C. Leonard, *ACS Catal.*, 2015, **5**, 6653–6657.
- A. Roldan and N. H. de Leeuw, *Faraday Discuss.*, 2016, **188**, 161–180.

