PHYSICAL CHEMISTRY OF NANOCLUSTERS AND NANOMATERIALS

NiS₂ Nanoparticles with Tunable Surface Area As Catalyst for Ethanol Oxidation

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Received March 2, 2018; revised March 2, 2018; accepted April 15, 2018

Abstract—NiS₂ is rationally and readily prepared via a simple and general hydrothermal synthetic route. The particle sizes of NiS₂ species are tunable by adjusting the pH value of the hybrid solution. The optimized sample (NiS₂-4) contains NiS₂ nanoparticles of about 32.6 nm, and large surface area of 368.5 m² g⁻¹. The high surface area renders NiS₂-4 an excellent electrocatalytic performance for ethanol oxidation. NiS₂-4 electrode also exhibits a good long-term cycling stability. 93.3% of the initial current density is recovered by moving the NiS₂-4 electrode into fresh 0.1 M NaOH solution with 0.5 M ethanol after 500 cycles. The excellent electrocatalytic properties of NiS₂-4 for ethanol oxidation stems from the high surface areas.

Keywords: NiS₂, surface area, mesopore, electrochemical catalyst, ethanol oxidation **DOI:** 10.1134/S0036024419080338

1. INTRODUCTION

In recent years, developing a clean and high-efficiency energy has triggered significantly interests to meet the requirements of sustainable society [1, 2]. Direct ethanol fuel cells (DEFCs) have become increasingly attractive owing to high energy conversion efficiency and low pollutant as well as the easy accessibility of ethanol [3]. In particular, Pt-based catalysts for DEFCs have shown ultrahigh electrocatalytic performance, higher energy conversion and excellent stability. However, the high cost of Pt-based catalysts inhibits its large scale applications [3, 4]. Hence, it becomes urgent to search for the alternative and inexpensive catalysts with good electrocatalytic properties. The designs of novel, effective and cheap electrocatalysts are still paramount challenging because of lack of excellent electrocatalytic activity and stability of the catalyst.

Given the electrocatalysts used in direct fuel cells, transition metal sulfides have attracted great attention due to their remarkable electronic, optical and catalytic properties [5]. So transition metal sulfides catalysts have been widely used in recent years and exhibited a better electrocatalytic activity among the non-noble materials for hydrogen evolution reaction, oxygen evolution and other catalysis [6–8]. For example, molybdenum sulfide (MoS_2) and many other transition metal sulfides have demonstrated promising catalytic activity in hydrogen evolution reaction [9–11].

Xie et al. studied defect-rich MoS_2 ultrathin nanosheets for hydrogen evolution, exhibits low onset overpotential, small tafel slope and excellent durability [9]. Moreover, Shen et al. fabricated an asymmetric supercapacitor used these unique $NiCo_2S_4$ hollow spheres, which delivers high energy and power densities and exhibits outstanding cycle life [12].

It is well known that surface area of electrocatalysts play an important role in catalytic activity and increasing the surface area of electrocatalysts has been proven as an effective strategy for enhancing electrochemical properties. Due to the higher surface areas bestow an open network for facile diffusion of fuels and products For example, [13-15]. the hierarchical NiCo₂O₄@Ni₃S₂ core/shell mesoporous nanothorn arrays exhibit high specific area, low charge transfer resistance and outstanding capacitance [13]. NiS₂ nanoparticles supported flower-like porous Al₂O₃ nanosheets exhibit high specific surface area of $383 \text{ m}^2 \text{ g}^{-1}$ and superior performances for hydrogen evolution reaction [14]. The porous $NiS_2//MoS_2$ exhibited superior catalytic performance, owing to the high surface area of 113 m² g⁻¹. The large surface area of NiS₂ spheres possibly provides more surface and small molecule access [15]. So NiS₂ materials have received much attention due to their excellent properties of high surface area and mesopores. However, the surface areas of the reported NiS_2 samples were less than 300 m² g⁻¹.

Herein, a novel oxidative ethanol catalyst has been successfully developed using high surface area mesoporous NiS₂ (368.5 m² g⁻¹) as catalytic materials. NiS₂ is rationally and readily prepared via a hydrothermal route. The method achieves a controllable BET surface area of the as-synthesized sample by adjusting pH value. The electrochemical performances of the NiS₂ catalysts were evaluated. The optimized sample of NiS₂-4 contains small NiS₂ pore width of 32.6 nm in size, large surface area of 368.5 m² g⁻¹. The high surface areas and abundant mesopores render NiS₂-4 an excellent electrocatalytic performance for ethanol oxidation and a good long-term cycling stability.

2. EXPERIMENT

2.1. Preparation of Catalysts

All reagents were of analytical grade without further purification and post-treatment. Distilled water was used in all experiments. In a typical synthesis of NiS_2 samples, 1.6 g sodium sulfide, 0.7 g nickel chloride was successively dissolved in 50 mL distilled water. The pH values were adjusted to 4-7. Subsequently, the mixtures solution was introduced into a 100 mL Teflon-lined autoclave. The reaction was kept at 120°C for 10 h, respectively. After cooling to room temperature, centrifugation treatment produced a series of products. The products were washed with 1.0 M HCl solution and deionized water for several times, and all of the samples were finally dried in a vacuum oven at 60°C overnight. The obtained samples with the different pH value were sequentially denoted as NiS₂-4, NiS₂-5, NiS₂-6, and NiS₂-7, respectively.

2.2. Characterization

The morphologies of the samples were studied by field-emission scanning electron microscope (FESEM, Hitachi S-4800). Hitachi H-7650 transmission electron microscope (TEM, operating voltage 100 kV), and JEOL JEM 2010 field emission transmission electron microscope (HRTEM, operating voltage 200 kV) were used to characterize the microstructures of the samples. The samples for TEM and HRTEM observations were prepared by dipping sonicated ethanol suspensions of powdery samples onto the copper grids. The phase identifications were carried out with powder X-ray diffraction (XRD) on a Bruker D8 Discover with Cu K_{α} radiation ($\lambda = 1.5418$ Å). The diffractions were collected in a two theta range of $10^{\circ}-80^{\circ}$ with a step of 0.02° and a rate of 8° min⁻¹. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 X-ray photoelectron spectrometer) was applied to investigate the compositions and chemical states. The nitrogen adsorption-desorption isotherms and the BrunauerEmmett-Teller (BET) surface area were measured at 77 K on a Micromeritics ASAP 2020M system.

2.3. Electrochemical Measurements

Cyclic voltammetry (CV) and chronoamperometric studies were performed using a CHI660D electrochemical workstation (Shanghai Chenhua, China), which were carried out in a conventional three-electrode electrochemical cell. A Pt wire, a saturated calomel electrode (SCE, 3 M KCl) and a glassy carbon electrode (GCE, a diameter of 3 mm) were used as the counter, reference and working electrodes, respectively. All potential values were referred to the SCE. Cyclic voltammetry (CV) and Chronoamperometry (CA) were used to study the activity and stability of the catalysts for ethanol oxidation reaction. The current densities were calculated using the geometrical area of the electrode. The glassy carbon electrode was mechanically polished with 50 nm gamma alumina powders, rinsed thoroughly with distilled water, and dried at room temperature. Electrochemical impedance spectroscopy (EIS) tests started from 100 kHz to 1 Hz with 5 mV potential amplitude. To prepare working electrode, a slurry was prepared by mixing 0.78 mg NiS₂ samples, 30 μ L Nafion solution, 270 μ L water, and 90 µL isopropyl alcohol. After sonicated for 30 min at room temperature, 10 μ L of the slurry was dropped on the active area of the glassy carbon electrode and then dried.

3. RESULTS AND DISCUSSION

3.1. Physical Characterization of As-Prepared Catalysts

The morphologies of the as-synthesized NiS₂ catalysts were characterized by SEM. NiS₂ catalysts are composed of dispersive particles of nanometer in sizes. All NiS₂ samples are aggregates of irregular particles with coarse surfaces. Figure 1a shows that the NiS₂-4 is dominated by small and uniform nanoparticles. The fundamental unit of these nanoparticles is an agglomerate rather than ultimate nanoparticle. Compared to the Fig. 1a, the Figs. 1b–1d shows the uniformity of NiS₂-5, NiS₂-6, and NiS₂-7 are slightly reduced because of the emergence of irregular shaped particles. And the aggregation with irregular structure is still the major product, demonstrating that it is a promising route for facile and scalable synthesis of high-purity NiS₂ without any additional procedure.

TEM test was carried out to further explore the microstructure of NiS₂-4 catalyst. The TEM image of the as-prepared NiS₂-4 catalyst in Fig. 2a clearly displays an irregular sphere structure with a diameter of about 150 nm. In inset of Fig. 2b, The distances of two adjacent lattice fringes are 0.283 and 0.327 nm, respectively, corresponding to the d-spacing of the (200) plane and the (111) plane of the NiS₂ [16].



Fig. 1. SEM images of NiS₂-4 (a), NiS₂-5 (b), NiS₂-6 (c), and NiS₂-7 (d) catalysts.



Fig. 2. TEM (a) and HRTEM (b) micrographs of the NiS₂-4 catalyst. The inset of Fig. 2b is the corresponding FFT of selected area.

Figure 3 shows the XRD patterns of the NiS₂ nanoparticles synthesized using different pH value. All the products display relatively smooth lines and sharp characteristic peaks at 31.5° , 35.3° , 38.8° , 45.1° , and 53.5° , corresponding to (200), (210), (211), (220), and (311) plane, respectively. All the peaks in the XRD patterns can be well indexed to NiS₂ (JCPDS no. 65-3325) [16, 17].

In order to investigate the specific surface area of the NiS₂ catalysts, N₂ absorption-desorption test was conducted. Figure 4a shows the typical type IV isotherms with the H3 hysteresis loop [14, 15]. This result proves the as-synthesized samples possess mesoporous structure. Moreover, the sharp increase of adsorptive quantities suggests the presence of the macropore and large-size mesopore at P/P_0 of more than



Fig. 3. (Color online) The XRD patterns for as-prepared NiS₂ catalysts.



Fig. 4. (Color online) (a) N_2 adsorption/desorption isotherms of NiS₂ catalysts and (b) BJH pore size distribution curves of NiS₂ catalysts.

0.9. The Barrett-Joyner-Halenda (BJH) pore-size distributions of all samples also confirm this result from Fig. 4b. NiS_2 -4 sample has wider mesopore size distribution in comparison with others samples. This structure of NiS_2 -4 sample is fit for a rapid mass transport process [18, 19].

The calculated parameters of pore structure are listed in Table 1 according to Fig. 4a. The Brunauer-Emmett–Teller (BET) surface areas are 368.5, 254.8, 206.7, and 129.4 m² g⁻¹ for NiS₂-4, NiS₂-5, NiS₂-6, and NiS_2 -7, respectively. Especially, the mesopore surface area of NiS₂-4, NiS₂-5, NiS₂-6, and NiS₂-7 are up to 215.8, 130.2, 118.3, and 80.7 $m^2 g^{-1}$, demonstrating that the low pH value can lead to a larger special surface area and mesoporous surface than the high pH values. The reason includes two aspects. Firstly, the reduced reaction rate due to the decreased concentrations of S²⁻ and OH⁻ ions in low pH value results the accumulation of more tiny particles. Besides, the higher pH value is, the larger the contents of nickel oxide and nickel hydroxide become. This derives from the competing reactions between Ni²⁺ ion and OH⁻ or S^{2-} ions. When pH value become highly, the higher proportional of nickel hydroxide and NiO can be formed with the markedly elevated concentrations of OH⁻ ion. After NiO and Ni(OH)₂ are removed by 1.0 M HCl solution, some macropores and mesopores are formed.

Table 1. Parameters of the pore structure of NiS_2 catalysts

Sample	$S_{\rm BET}, {\rm m}^2 {\rm g}^{-1}$	$S_{\rm meso},{\rm m}^2{\rm g}^{-1}$	D, nm
NiS ₂ -4	368.5	215.8	32.6
NiS ₂ -5	254.8	130.2	20.8
NiS ₂ -6	206.7	118.3	28.3
NiS ₂ -7	129.4	80.7	21.7

 S_{BET} , BET specific surface area; S_{meso} , BJH mesopore surface area; D, adsorption average pore diameter.

3.2. Electrochemical Performances of As-Prepared Catalysts

In Fig. 5a, a pair of obvious redox peaks at 0.42 and 0.3 V can be clearly seen, which derives from the redox reaction between NiS₂ and NiS₂OH, as shown in Eq. (1) [17]. As is well known, the anodic peak potential of NiO to NiOOH located at 0.35 V [20]. Moreover, the current densities on the NiO or Ni(OH)₂ electrodes is markedly less than those of NiS₂ electrodes. Therefore, no oxidative current peaks of NiO or Ni(OH)₂ are observed. In Fig. 5a, NiS₂-4 electrode exhibits a lower onset potential and higher current density in comparison with others catalysts. This result correlates with larger specific surface area of BET and higher content of NiS₂ for NiS₂-4 sample.

$$NiS_2 + OH^- \leftrightarrow NiS_2OH + e^-,$$
 (1)

$$NiS_2OH/NiOOH + ethanol$$

$$\leftrightarrow NiS_2/NiO + products.$$
(2)

In Fig. 5b, the oxidative current densities of NiS₂ to NiS₂OH for the same catalyst enormously increase in 0.1 M NaOH solution with 0.5 M ethanol compared with 0.1 M NaOH solution, but the reductive current densities have scarce change. This indicates ethanol remarkably accelerates oxidative reaction of NiS₂ to NiS₂OH because oxidative reaction of ethanol is generated by NiS₂OH oxidant, as observed as Eq. (2). Hence, NiS₂ can be used as an effective catalyst of ethanol oxidation.

Besides, it is found that the enclosed area of CV loop of the NiS₂-4 is larger than the others. Therefore, the current densities of the NiS₂-4 are higher than the others, implying its better electrochemical reactivity [16]. Figure 5b shows the corresponding CVs in 0.1 M NaOH + 0.5 M C₂H₅OH for the catalysts. It can be clearly seen that NiS₂-5, NiS₂-6, and NiS₂-7 catalysts show a mildly ascending oxidation peak current density, while NiS₂-4 catalyst gives an enhanced anodic peak at +0.55 V (vs. SCE), showing 2 times higher cat-

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Fig. 5. (Color online) CV curves of NiS₂ electrodes in 0.1 M NaOH solution without (a) and with (b) 0.5 M ethanol at the scan rate of 50 mV s⁻¹.



Fig. 6. (Color online) (a) CVs of NiS₂-4 catalyst in 0.1 M NaOH solution containing different ethanol concentrations (0-1 M) at a scan rate of 50 mV s⁻¹. Inset image: dependency of the anodic peak currents density on the concentration of ethanol in solution; (b) CA curves of NiS₂-4 catalyst in 0.1 M NaOH solution in the presence of ethanol with various concentrations of (1) 0, (2) 0.1, (3) 0.3, and (4) 0.5 M, respectively. Inset: (A) dependence of $I_{\text{catal}}/I_{\text{L}}$ vs. $t^{1/2}$ derived from the data of chronoamperograms of 4 panel and (B) dependency of transient current density on $t^{-1/2}$.

alytic activity for ethanol oxidation in comparation with NiS₂-7 catalyst. Thus, with the different pH value in the synthesis environment, the catalysts suggest a higher current response and a lower current response, indicating an optimized pH can cause electronic effect and allow the nickel to reach a higher oxidation state during the oxidation process [20]. Apart from current density, the onset potential for catalysts is another significant parameter. The onset potentials of the NiS₂-4, NiS₂-5, NiS₂-6, and NiS₂-7 catalysts are measured to be at about 0.35, 0.36, 0.37, and 0.39 V (vs. SCE), respectively. The lower onset potential of NiS₂-4 catalyst further indicates the appropriate pH can promote the electron transfer for ethanol oxidation.

It is strongly preferable to use high concentration ethanol, which can be attributed to enhance the power density and simultaneously diminish the cells size [21]. As shown in Fig. 6a, it is found that current densities increase with the increasing concentration of ethanol in the initial stage of the backward scan, explaining that ethanol molecules could not be completely oxidized in the forward scan and have to continue to be oxidized at the high potential in the backward scan.

Double steps chronoamperometry of NiS₂-4 catalyst is also conducted in different ethanol concentrations (Fig. 6b). The polarization current densities of NiS₂-4 catalyst decreases rapidly at the initial stage within 20 s and then quickly tends to be stable. Besides, the current densities of NiS₂-4 catalyst increase obviously with the elevated ethanol concentration at the potential of 0.53 V, suggesting that the NiS₂-4 electrode has a stable electrocatalytic activity for ethanol oxidation.

Calculations on the basis of the chronoamperogram curves readily derive the rate constant (k) of the electrocatalytic ethanol oxidation according to Eq. (3) [20].



Fig. 7. CV curves (a) of NiS₂-4 catalyst measured at different cycles in 0.5 M ethanol. Nyquist diagrams (b) of the NiS₂-4 catalyst in different concentration of ethanol solution.

$$\frac{I_{\text{catal}}}{I_{\text{L}}} = (\pi k C t)^{1/2}, \qquad (3)$$

where, I_{catal} and I_{L} sequentially represent the currents of the electrodes in the presence and absence of ethanol, k is the catalytic reaction rate constant, C is the ethanol concentration, and t is the elapsed time. From the slope of $I_{\text{catal}}/I_{\text{L}}$ vs. $t^{1/2}$ plot (inset A in Fig. 6b), the k value for NiS₂-4 electrode in the presence of 0.5 M ethanol, is calculated to be 3019 cm³ mol⁻¹ s⁻¹. Inset B Fig. 6b presents the linear dependence of current density and $t^{-1/2}$, demonstrating that the reaction process is dominantly controlled by diffusion [20].

The stability of NiS₂-4 catalyst for ethanol oxidation is tested by the continuous CV measurements in 0.1 M NaOH solution with 0.5 M ethanol. As is shown in Fig. 7a, the current densities remain 90.1% after 500 cycles. The declined current densities possibly stem from the reduced ethanol concentration. To prove this conclusion, a CV test is carried out by moving the NiS₂-4 catalyst into fresh 0.1 M NaOH solution with 0.5 M ethanol after 500 cycles. The CV data shows that the recovery ratio of the oxidative peak current density is up to 93.3%. The high retention rate of long cycling process and reversible peak current density implies a good cyclic stability of NiS₂-4 catalyst for ethanol oxidation.

The charge transfer resistance (R_{ct}) of ethanol oxidation on electrode is one of the most important parameters of electrocatalyst. Electrochemical impedance spectroscopy (EIS) is a powerful method for studying the R_{ct} of electrode. Figure 7b shows the Nyquist diagrams of NiS₂-4 electrode recorded at 0.5 V (vs. SCE) with concentrations range between 0 and 0.5 M of ethanol in 0.1 M NaOH solution.The Nyquist plots of the NiS₂-4 electrode exhibit two partially overlap squeezing capacitive loops in high and low frequencies. The squeezing capacitive loop of electrodes in high frequencies can be related to the combination of the R_{ct} of transformation between Ni³⁺ and Ni²⁺ on the surface [5, 22]. The Nyquist plots follow another small capacitive loop in low frequencies, especially these of electrodes in 0.3 and 0.5 M of ethanol solution, which is attributed to the absorbed intermediate products [22]. In addition, the diameters of the semi-circle become smaller with the increase of ethanol concentration in high frequencies for NiS₂-4 electrode. These mean that the R_{ct} of ethanol oxidation on electrode decrease with the rise of ethanol concentration.

The excellent electrocatalytic activity of NiS_2 -4 catalyst stems from the unique structures. A large number of pores supply a high special surface area and more active sites. The mesopores also facilitate the ethanol diffusion. As well, NiS_2 -4 catalyst offers more pure NiS_2 . These structural features bestow NiS-4 catalyst an enhanced electrocatalytic performances for ethanol oxidation, including higher current density, low onset potential and excellent cycling stability.

4. CONCLUSION

In this work, a new non-noble electrocatalyst for DEFCs was prepared by a facile, economic, and environmentally friendly method. The surface area and sizes of NiS₂ are controlled by the pH value. The asprepared NiS₂ catalysts exhibit a higher catalytic activity for ethanol oxidation in alkaline medium. The NiS₂-4 catalyst has the best catalytic activity for ethanol oxidation due to high special surface area, more active sites and abundant mesopores. The optimized sample of NiS₂-4 catalyst exhibits a high electrocatalytic activity and long-term stability for ethanol oxidation in alkaline solution.

ACKNOWLEDGMENTS

This research was supported by Natural Science Foundations of Tianjin (nos. 15JCQNJC05700, 17JCTPJC47300, and 17JCQNJC06100), Natural Science Foundations of China (nos. 21271138 and 21703152), and the State Key Laboratory of Inorganic Synthesis and Preparative Chemistry of Jilin University (no. 2015–02).

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