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Article

Synthesis of silk-like FeS₂/NiS₂ hybrid nanocrystals with improved reversible oxygen catalytic performance in a Zn-air battery

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ABSTRACT

The development of highly active and stable reversible oxygen electrocatalysts is crucial for improving the efficiency of metal-air battery devices. Herein, an efficient liquid exfoliation strategy was designed for producing silk-like FeS₂/NiS₂ hybrid nanocrystals with enhanced reversible oxygen catalytic performance that displayed excellent properties for Zn-air batteries. Because of the unique silk-like morphology and interface nanocrystal structure, they can catalyze the oxygen evolution reaction (OER) efficiently with a low overpotential of 233 mV at $j = 10 \text{ mA cm}^{-2}$. This is an improvement from the recently reported catalysts in 1.0 M KOH. Meanwhile, the oxygen reduction reaction (ORR) activity of the silk-like FeS₂/NiS₂ hybrid nanocrystals showed an onset potential of 911 mV and a half-wave potential of 640 mV. In addition, the reversible oxygen electrode activity of the silk-like FeS₂/NiS₂ hybrid nanocrystals was calculated to be 0.823 V, based on the potential of the OER and ORR. Further, the homemade rechargeable Zn-air batteries using FeS₂/NiS₂ hybrid nanocrystals as the air-cathode displayed a high open-circuit voltage of 1.25 V for more than 17 h and an excellent rechargeable performance for 25 h. The solid Zn-air batteries exhibited an excellent rechargeable performance for 15 h. This study provided a new method for designing interface nanocrystals with a unique morphology for efficient multifunctional electrocatalysts in electrochemical reactions and renewable energy devices.

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1. Introduction

Recently, electrocatalysts have become of great interest in electrochemical reactions owing to their role in renewable energy conversion and storage systems, such as water splitting, metal-air batteries, and ion storage [1–3]. Oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) are the most significant and basest electrochemical reactions in the renewable energy system

[4–6]. In addition, the OER and ORR performances indicate a reversible oxygen catalytic activity, which demonstrates the properties of metal-air batteries, such as Zn-air, Li-air, and Na-air batteries [7–9]. Traditionally, the best electrocatalysts for OER are Ir, Ru, and their oxides, and Pt is the most efficient one for ORR and HER. However, they are not widely used in industry, which can be attributed to high cost, scarcity, and poor durability [10]. Therefore, the design of ideal electrocatalysts based on inexpensive elements with a high current density

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ty at a low overpotential and long-term stability is important for the development of renewable energy systems [11]. To address these challenging issues, various transition-metal based catalysts and methods have been designed for the energy reactions, such as perovskite, metallic oxide, and their derivatives [12–20]. However, exploring efficient strategies to develop more active and stable electrocatalysts in a more economical way is still a scientific task in the development of renewable energy systems.

Transition metal dichalcogenides (TMDs), especially ultrathin nanosheets, such as MoS_2 , TiS_2 , TaS_2 , WS_2 , MoSe_2 , WSe_2 , etc., have received increasing research interest in the HER in recent years for their ideal atomic arrangements and high electrical conductivities [21–25]. In addition, many reports have stated that only the surface atoms of the TMD electrocatalysts can act as the active sites for the HER [26,27]. Nevertheless, the reversible oxygen electrocatalytic performance of these TMDs is limited because it is difficult to develop effective strategies to tune their electronic structures. Recently, researchers have found that fabricating the nanointerface is an efficient way to optimize the electronic structure of various materials [15,16]. The interface nanomaterials show optimized adsorption of the oxygen species (OH^- , O_2) and more catalytic sites for the different domains between the interface, which is crucial for electrocatalytic performance.

In this study, an efficient liquid exfoliation strategy was developed using formamide as the stripping reagent under continuous ultrasonic treatment (Scheme 1). The obtained $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals showed two phase compositions and silk-like morphologies, which were confirmed using X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals exhibited enhanced reversible oxygen catalytic performance with a low overpotential of 233 mV at $j = 10 \text{ mA cm}^{-2}$ for the OER. This was an improvement over the recently reported relevant catalysts in 1.0 mol/L KOH with an onset potential of 911 mV and a half-wave potential of 640 mV for the ORR. Further, according to the potential of the OER and ORR, the reversible

oxygen activity of the silk-like $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals was calculated to be 0.823 V. Based on the excellent reversible oxygen performance, the homemade rechargeable Zn-air batteries using $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals as the air-cathode displayed a high open-circuit voltage (OCV) of 1.25 V for more than 17 h and an excellent rechargeable performance for 25 h. In addition, the solid Zn-air batteries were successfully fabricated with an excellent rechargeable performance of approximately 15 h. This study provided a new method for designing interface nanocrystals with a unique morphology as efficient electrocatalysts for renewable energy systems.

2. Experimental

2.1. Synthesis of the NiFe_2O_4 nanocrystals

The NiFe_2O_4 nanocrystals were obtained according to a previous study [13].

2.2. Synthesis of the $\text{FeS}_2/\text{NiS}_2$ bulk nanocrystals

In a typical procedure, the NiFe_2O_4 nanocrystals were placed in a tube and heated to 500 °C with a rate of 10 °C min^{-1} under a flowing N_2 atmosphere. After reacting for 2 h at 500 °C, the system was cooled under a flowing N_2 atmosphere to room temperature naturally [15,16].

2.3. Synthesis of the silk-like $\text{FeS}_2/\text{NiS}_2$ nanocrystals

The $\text{FeS}_2/\text{NiS}_2$ bulk powder (10 mg) was dispersed in formamide (30 mL) and ultrasonically treated in water with ice for more than 3 h. The silk-like $\text{FeS}_2/\text{NiS}_2$ nanocrystals and un-exfoliated product were obtained by centrifuging the solution at different rotational speeds, and then the solution was dried in a vacuum at 50 °C [17].

2.4. Structure characterization

XRD experiments were conducted using an X'Pert Pro X-ray

Scheme 1. Schematic of the synthetic procedures of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals.

diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm) under a voltage of 40 kV from 20° to 90° . TEM and HRTEM observations were performed under an acceleration voltage of 200 kV with a JEOL JEM 2100 TEM. (XPS) analyses were performed with a VG ESCALAB 220I-XL device and corrected with a C 1s line at 284.6 eV.

2.5. OER test

All the electrochemical measurements were carried out in a three-electrode system consisting of a working electrode made by the corresponding catalysts, a Pt auxiliary electrode, and an Hg/HgO reference electrode connected to a CHI 760 E electrochemical workstation (CHI Instruments, Shanghai Chenhua Instrument Corp., China) at a scan rate of 2 mV s^{-1} in 1.0 mol/L KOH solution. The potentials were referenced to RHE ($E(\text{RHE}) = E(\text{Hg/HgO}) + 0.0951\text{pH} + 0.098$). In addition, a resistance test was performed, and the iR compensation was applied using CHI software. In this study, the electrochemical experiments were conducted at $20 \pm 0.2^\circ\text{C}$.

2.6. ORR test

The electrochemical measurements for the ORR were conducted on a rotating ring-disk electrode (RRDE) at 1600 rpm in an oxygen-saturated KOH solution (0.1 mol/L). The ring-disk electrode (RDE) was measured at the rotating rates of 400–2400 rpm at the scan rate of 2 mV s^{-1} . The relationship between the measured currents (j) with various rotating speeds (ω) under fixed potentials was expressed on the basis of the K-L equation [15,16].

$$1/j = 1/j_k + 1/(B\omega^{1/2}) \quad (1)$$

The parameter j_k is the kinetic current, and ω is the electrode rotating rate. The parameter B is determined from the slope of the K-L plots based on the Levich equation below.

$$B = 0.2nF(D_{\text{O}_2})^{2/3} \nu^{-1/6} C_{\text{O}_2} \quad (2)$$

2.7. Battery test

The Zn-air battery was assembled by the zinc plate anode. 25–30 mL of 6.0 mol/L KOH solution were used as the electrolyte without a separator. All the Zn-air batteries were tested under an ambient atmosphere. The polarization curve measurements were performed by LSV (2 mV s^{-1}) at 25°C with a CHI 760 E electrochemical working station (CH Instrument). The current and power densities were normalized to the effective surface area of the air-cathode electrode [15,16].

3. Results and discussion

3.1. Characterization of the silk-like $\text{FeS}_2/\text{NiS}_2$ nanocrystals

Ultrasonic assisted liquid phase exfoliation was successfully developed to prepare the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals (Scheme 1) [15–17]. Fig. 1(a) shows the XRD pattern of the obtained $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals. The peaks of $\text{FeS}_2/\text{NiS}_2$ were attributed to FeS_2 and NiS_2 , which belonged

Fig. 1. XRD patterns (a) and TEM (b, c) and HRTEM (d) images of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals.

to the space groups of P1 (JCPDS card no. 71–1680; $a = b = c = 5.417 \text{ \AA}$) with a triclinic structure and Pa3 (JCPDS card no. 11–99; $a = b = c = 5.670 \text{ \AA}$) with a cubic structure, respectively. The XRD pattern showed the hybrid structure for the two different phases. In addition, the XRD patterns of the single FeS_2 and NiS_2 are shown in Figs. S1 and S2. The TEM images were measured to conform the morphology of the $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals. Figs. 1(b) and (c) show the TEM images of the $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals, illustrating the silk-like structure. The HRTEM image of the $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals (Fig. 1(d)) showed two different domains of FeS_2 and NiS_2 , in which the clearly identified lattice fringe spaces of 2.71 and 2.83 $\text{\AA}$ corresponded to the same (200) plane of the triclinic FeS_2 and cubic NiS_2 .

3.2. Surface structural properties of $\text{FeS}_2/\text{NiS}_2$

The surface properties of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals were investigated using the X-ray photoelectron spectra (XPS) measurements. Fig. 2(a) shows the Fe $2p$ spectra of the $\text{FeS}_2/\text{NiS}_2$ and FeS_2 nanocrystals. The $2p_{3/2}$ shows an obvious shift of approximately 0.49 eV from 706.89 eV for FeS_2 to 707.38 eV for $\text{FeS}_2/\text{NiS}_2$, indicating the enhanced oxidizability of the interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals [15]. The same results were found in the Ni $2p$ spectra (Fig. 2(b)). The Ni also showed a higher oxidation state in the interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals for the $2p_{3/2}$ shift of approximately 0.34 eV from 853.43 eV for NiS_2 to 853.77 eV for $\text{FeS}_2/\text{NiS}_2$. The S $2p$ spectra of those catalysts also showed the same changes. As shown in Fig. 2(c), the S $2p$ spectra of FeS_2 and NiS_2 contained the same peak position at 162.40 eV; however, after the fabrication of the nanointerface, the S $2p$ spectra show obvious about 0.48 eV from the single phase to the interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals (162.87 eV). Based on the above analysis and experiment, the fabrication of the nanointerface enhanced the coupling between the different domains, which could further improve the electronic transfer ability.

Fig. 2. XPS spectra of Fe 2p (a), Ni 2p (b), and S 2p (c) for the obtained catalysts.

3.3. OER performance of FeS₂/NiS₂

The OER activity of the catalysts was evaluated using a linear scan voltammogram (LSV) in 1.0 mol/L KOH at the scan rate of 2 mV s⁻¹ [15,16]. The silk-like interface FeS₂/NiS₂ hybrid nanocrystals exhibited greater OER activity than that with the FeS₂ and NiS₂ nanocrystals. In Fig. 3(a), the OER current increased under the silk-like interface FeS₂/NiS₂ hybrid nanocrystals catalyzed and more quickly than other prepared catalysts. The onset potential of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals for the OER was 92 mV, which was better than those of FeS₂ (221 mV) and NiS₂ (227 mV), and the overpotential at the OER current density of 10 mA cm⁻² for the in-

terface FeS₂/NiS₂ hybrid nanocrystals was 233 mV lower than those of FeS₂ (285 mV) and NiS₂ (346 mV). The silk-like interface FeS₂/NiS₂ hybrid nanocrystals could maintain stability for more than 30 h (Fig. S3). The Tafel slopes were further confirmed to determine the reaction kinetics for the OER. As shown in Fig. 3(b), the silk-like interface FeS₂/NiS₂ hybrid nanocrystals displayed the lowest Tafel slope of 64 mV dec⁻¹ for the OER. This was smaller than those of FeS₂ (137 mV dec⁻¹) and NiS₂ (196 mV dec⁻¹). In addition, the silk-like interface FeS₂/NiS₂ hybrid nanocrystals showed excellent OER activity, more than those of the FeNi based electrocatalysts (Fig. 3(c)), such as NiFe LDH, Fe₇S₈ bulk, NiFe alloy/NiFe₂O₄, etc. [28–34]. Fig. 3(d) shows several important parameters for the OER, suggesting a superior activity of the silk-like interface

Fig. 3. LSV (a) and Tafel (b) slopes of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals, FeS₂, and NiS₂. Images (c) and (d) show the OER activity comparison of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals and other catalysts.

Fig. 4. LSV (a), K-L plots (b), Tafel slopes (c), and parameter comparison (d) of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals, FeS₂, and NiS₂ for the ORR in 0.1-M KOH. The inset in (b) shows the kinetic current densities and the electron transfer numbers (on the top of the rectangular bars) for the ORR on the catalysts.

FeS₂/NiS₂ hybrid nanocrystals compared to those of the other obtained catalysts.

3.4. ORR performance of FeS₂/NiS₂

The ORR activity of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals, FeS₂, and NiS₂ were further explored in 0.1 mol/L KOH [15]. As shown in Fig. 4(a), the silk-like interface FeS₂/NiS₂ hybrid nanocrystals showed a more repaid catalytic speed and lower potential. The onset potential (E_{Onset} : 0.91 V) and half-wave potential ($E_{1/2}$: 0.64 V) of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals were similar to those of the benchmarked Pt/C (onset potential: 0.95 V, halfwave potential: 0.78 V) [15] and superior to those of FeS₂ (E_{Onset} : 0.804 V and $E_{1/2}$: 0.553 V) and NiS₂ (E_{Onset} : 0.853 V and $E_{1/2}$: 0.632 V). In addition, it had good stability (Fig. S4). Then, the electron transfer number (n) was investigated. In Fig. 4(b), the Koutechy-Levich (K-L) plots were calculated to confirm the electron transfer number of the obtained catalysts for the ORR, according to the LSV curves at different rotating rates (Fig. S5). The electron transfer number of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals was approximately 4.15, and the kinetic current density (j_k) of 19.6 mA cm⁻² (inset of Fig. 4(b)) was better than those of FeS₂ (n : 3.9 and j_k : 16.7 mA cm⁻²) and NiS₂ (n : 3.66 and j_k : 15.6 mA cm⁻²), based on the K-L equation (experimental part). These results indicated the superior ORR catalytic activity through a four-electron pathway of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals. Further, the

Tafel slopes were calculated to confirm the reaction kinetics. As shown in Fig. 4(c), the silk-like interface FeS₂/NiS₂ hybrid nanocrystals displayed a lower Tafel slope of 73 mV dec⁻¹ for the OER, which was smaller than those of FeS₂ (121 mV dec⁻¹) and NiS₂ (152 mV dec⁻¹) and was approaching that of Pt/C [35,36]. Fig. 4(d) shows several important parameters for the ORR. The silk-like interface FeS₂/NiS₂ hybrid nanocrystals exhibited excellent ORR performance in a basic media.

3.5. Reversible oxygen activity of NiO/CoN PINWs

Based on the above analysis and experimental results, the silk-like interface FeS₂/NiS₂ hybrid nanocrystals exhibited excellent bifunction for the OER and ORR (Fig. 5). Furthermore, the reversible oxygen electrode activity of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals was confirmed according to the different OER and ORR metrics, which could be calculated by the equation below [15].

$$\Delta E = E_{j=10} - E_{1/2} \quad (3)$$

The silk-like interface FeS₂/NiS₂ hybrid nanocrystals exhibited a ΔE value of 0.823 V (insert in Fig. 5), which was less than those of Pt/C (1.13 V) [15], FeS₂ (0.944 V), and NiS₂ (0.962 V), indicating better reversible oxygen activity of the silk-like interface FeS₂/NiS₂ hybrid nanocrystals and a potential application in metal-air batteries.

3.6. Performance of the liquid Zn-air Battery

Fig. 5. Reversible oxygen catalytic performance of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals, FeS_2 , and NiS_2 . The insert shows the important parameters for reversible oxygen activity.

Considering the excellent bifunctional catalytic and reversible oxygen performance of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals, a homemade Zn-air battery was assembled to further identify its performance under practical battery operational conditions. This battery used a zinc plate as the anode, silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals as the air-cathode, and 6.0 mol/L KOH as the electrolyte (insert in Fig. 6(a)) [15,16]. The fabricated battery operated stably with a high OCV of 1.25 V for more than 17 h (Fig. 6(a)). The maxi-

mum power density of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals was 26 mW cm^{-2} at 70.8 mA cm^{-2} (Fig. 6(b)), which was greater than those of FeS_2 (16.7 mW cm^{-2} at 35.89 mA cm^{-2}) and NiS_2 (6.8 mW cm^{-2} at 41 mA cm^{-2}). As shown in Fig. 6(c), a lower charge-discharge voltage gap was observed for the Zn-air battery with the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals as the air-cathode than those of FeS_2 and NiS_2 , indicating a better recharge ability and a good capacity (Fig. S6). Further, the battery cycling test was performed to confirm the recharge ability of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals. The ideal reversible oxygen catalysts should possess a low charging voltage (E_{charging}), high discharging voltage ($E_{\text{discharging}}$), and minimal fluctuation of E_{charging} and $E_{\text{discharging}}$. As expected, the battery fabricated with the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals showed a stable charging voltage at different current densities for approximately 25 h (Fig. 6(d)), indicating an excellent recharge ability of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals in the Zn-air battery.

3.7. Performance of the solid Zn-air battery

Furthermore, solid Zn-air batteries based on the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals were fabricated. As shown in Fig. 7(a), the flexible solid Zn-air batteries were built using a zinc anode, hydrogel polymer electrolyte, catalyst cathode, and nickel foam (NF) air-collector [15,16]. The re-

Fig. 6. (a) OCV curve of the Zn-air batteries fabricated with the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals. Image (b) shows the polarization and power density curves, and image (c) shows the charge and discharge polarization curves of the Zn-air batteries fabricated using the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals, FeS_2 , and NiS_2 . Image (d) shows the galvanostatic discharge-charge cycling curves at 1 and 3 mA cm^{-2} of the rechargeable Zn-air batteries fabricated with the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals. The inset in (a) shows the schematic of the liquid Zn-air battery.

Fig. 7. (a) Flexible solid Zn-air batteries using the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals as the air-cathode catalyst. Image (b) shows the open-circuit plots of the single and three-series solid batteries with the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals. Image (c) shows the galvanostatic discharge-charge cycling curves of the portable Zn-air battery at the current densities of 3 and 5 mA cm^{-2} . Image (d) shows a photograph of a green LED (approximately 3.0 V) powered by three-series solid Zn-air batteries.

charge ability of the flexible solid Zn-air batteries was confirmed. Fig. 7(b) shows the OCV of the single battery (1.24 V and more than 15 h). The OCV for three-series solid batteries is 3.72 V and more than 7 h. As shown in Fig. 7(c), the discharge/charge cycles for the solid battery were maintained for 15 h at the current densities of 0.5 and 1 mA cm^{-2} (10 min per cycle), indicating excellent performance of the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals fabricated flexible solid Zn-air batteries. In addition, as shown in Fig. 7(d), a green LED (approximately 3.0 V) was powered by three-series solid Zn-air batteries using the silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals as the air-cathode.

4. Conclusions

In summary, silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals were prepared by an efficient liquid exfoliation strategy using formamide as the stripping reagent and a continuous ultrasonic treatment. The obtained hybrid nanocrystals showed an interface structure for two domains of FeS_2 and NiS_2 in the HRTEM image and a unique silk-like morphology. The silk-like interface $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals showed enhanced electrocatalytic performance with a low overpotential of 233 mV at $j = 10 \text{ mA cm}^{-2}$ for the OER and an onset potential of 911 mV and half-wave potential of 640 mV for the ORR. Further, the silk-like $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals also exhibited

excellent reversible oxygen activity for the small ΔE of 0.823 V. In addition, based on the excellent reversible oxygen performance, the homemade rechargeable Zn-air batteries using $\text{FeS}_2/\text{NiS}_2$ hybrid nanocrystals as the air-cathode displayed a high OCV and excellent rechargeable performance. The method designed in this study could be used for designing other interface nanocrystals with a unique morphology for potential applications in renewable energy systems.

Nomenclature

j_k	kinetic current, mA cm^{-2}
ω	electrode rotating rate, rpm
B	slope of the K-L plots
n	transferred electron number per oxygen molecules
F	Faraday's constant, $96485.3 \text{ C mol}^{-1}$
D_{O_2}	diffusion coefficient of O_2 in 0.1 mol/L KOH, $D_{\text{O}_2} = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
C_{O_2}	bulk concentration of O_2 , $C_{\text{O}_2} = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$
ν	kinetic viscosity, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$
$E_{j=10}$	OER potential at a current density of 10 mA cm^{-2} , V
$E_{1/2}$	ORR potential taken at the half wave, V

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Graphical Abstract

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Synthesis of silk-like FeS₂/NiS₂ hybrid nanocrystals with improved reversible oxygen catalytic performance in a Zn-air battery

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Herein, an efficient liquid exfoliation strategy was designed for producing silk-like FeS₂/NiS₂ hybrid nanocrystals with enhanced reversible oxygen catalytic performance that displayed excellent properties for Zn-air batteries.

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可逆氧催化性能提升的FeS₂/NiS₂纳米复合物的合成及其在锌空电池中的应用

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摘要: 当今世界环境与能源问题仍广受关注, 我们所依赖的燃料电池大部分依然是不可再生的能源, 如煤、石油、天然气等化石燃料, 且在使用过程中产生大量的有毒有害气体, 造成酸雨、温室效应等不良后果, 对环境造成严重的影响. 因此, 寻找一种可替代化石燃料、环境友好且可再生的新能源燃料意义重大. 新型高效稳定的可逆氧催化材料在可再生能源, 如锌空电池的应用中具有重要作用, 而这种电池是一种可再生的新型能源, 对环境友好. 因此, 本文设计了一种具有优良的可逆氧催化性能的材料.

首先通过水热法合成NiFe₂O₄前驱体, 然后在管式炉中对其进行高温硫化, 最后采用超声辅助液相剥离法制备了丝状界面FeS₂/NiS₂复合纳米材料. 所合成的催化剂具有独特的丝状形貌和界面, 因而具有优良的双功能电催化性能和可逆氧催化性能. 对于氧析出反应(OER), 该材料具有较低的电势, 仅需233 mV过电势即可实现析氧电流10 mA cm⁻², 该性能优于大多数报道的NiFe催化材料的性能; 同时, 该材料对氧还原反应(ORR)也具有很好的催化效果, 其中ORR反应的起始电压为911 mV, 半波电位为640 mV. OER和ORR催化活性结果表明, 该材料具有优良的可逆氧催化性能, 其 ΔE 值为0.823 V, 优于贵金属催化材料. 基于此, 我们设计组装了液态和固态的锌空电池, 并进行一系列的测试. 结果表明, 该系列电池在测试条件下均具有较高的开路电压和优良的充放电能力, 并且在固态的锌空电池上表现出很好的可弯曲性, 使其成为一种非常好的可折叠柔性固态锌空电池, 具有更广泛的应用前景. 这也为传统过渡金属催化材料的设计合成提供了新思路: 在传统过渡金属的基础上, 可通过更加新颖的合成方法使其具有独特的形貌, 乃至非常好的双功能催化性和可逆氧催化性能, 从而推动锌空电池的发展. 另外, 本文所设计的固态柔性锌空电池模型也可为相关设计应用提供参考.

关键词: 丝状; FeS₂/NiS₂; 界面; 可逆氧催化; 锌空电池

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