NiCo$_2$S$_4$-Based Materials for Electrochemical Applications

Ming Sun,* Jinjin Tie, Yao Li, and Lin Yu

Key Laboratory of Clean Chemistry Technology of Guangdong Regular Higher Education Institutions, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong510006, China

NiCo$_2$S$_4$ has attracted worldwide attention in the field of energy storage/conversion. In this paper, we summarize the up-to-date progress on the preparation strategies, the applications as electrode materials for supercapacitors, lithium-ion batteries and dye sensitized solar cells, as well as electrocatalysts for the hydrogen evolution reaction, oxygen reduction reaction and oxygen evolution reaction. We also discuss the strategies to improve the electrochemical performance, and future trends of the NiCo$_2$S$_4$-based materials.

**Keywords** NiCo$_2$S$_4$, energy storage, preparation

**Introduction**

In the past decades, the issue of environment pollution and energy crisis makes the research of renewable, green energy to be a hot topic. The energy includes wind energy, solar energy, hydrogen energy, biomass-based energy, etc. For better applications of such energy, it is necessary to develop the technologies and equipments concerning on energy storage and conversion, for example, supercapacitors (SCs), lithium-ion batteries (LIBs), metal-air batteries, and fuel-cells. The electrode materials or electrode catalysts are crucial for the above energy devices, and their performances are largely determined by the materials. Therefore, much attention has been paid on the rational design and preparation of electrode materials or electrode catalysts with excellent properties and activities.

Figure 1 The papers on NiCo$_2$S$_4$ published in recent 5 years (until September in 2017).

NiCo$_2$S$_4$ is a typical representation of the functional materials used for energy application, and it has been heavily studied across many field. We have used “NiCo$_2$S$_4” as a key word, and searched the paper published in Web of Science (until September in 2017). Figure 1 shows that the research on NiCo$_2$S$_4$ has a blowout growth. The wide attention and application is related with its inherent advantages and special physical-chemical properties. NiCo$_2$S$_4$ has a thiospinel structure with Ni and Co occupying tetrahedral sites and octahedral sites, respectively. It is speculated that the outstanding electrochemical activity is related with the following facts: metallic conductivity ($1.25\times10^6$ S m$^{-1}$), good redox chemistry, rich in composition and morphology.

Till date, NiCo$_2$S$_4$ with various morphology and architectures has been reported and widely used in the area of SCs, LIBs, metal-air batteries, and fuel-cells. Herein, we make a brief review and discussion on the preparation, application, and the strategies to enhance the activity of NiCo$_2$S$_4$. We also discuss the future challenges and perspectives of the NiCo$_2$S$_4$ materials.

**Synthetic strategies for NiCo$_2$S$_4$**

Generally, to prepare NiCo$_2$S$_4$ materials, there are three kind of routes: one-step, two-step and three step routes. The one-step method is easy by the reaction among Ni$^{2+}$, Co$^{2+}$ and different sulfur. Sometimes, impurities such as Co$_2$S$_3$ could be introduced. To avoid the impurities, it is better to use relatively higher hydrothermal temperature and longer reaction time. The one-step method usually involves with the hydrothermal process. However, there are also electrodeposited method reported.

Most of the publications on NiCo$_2$S$_4$ involve with the two-step procedure: formation of NiCo(OH)$_{2-x}$CO$_3$ $[0\leq x \leq 1]$ by Ni$^{2+}$, Co$^{2+}$ and different alkali (OH, NH$_3$·H$_2$O, NH$_4$F, urea, organic base such as hexamethylenetetramine), then converting it into NiCo$_2$S$_4$ by ion-exchange reaction using different S sources such as Na$_2$S, NaHS, S, H$_2$S or organic sulfur (thiourea, thiosemicarbazide). Most of the first and second steps are usually via the hydrothermal process. The two-way method is complicated. However, using this method, we can tune the morphology of NiCo(OH)$_{2-x}$CO$_3$ by different salt of Ni and Co (Cl, NO$_3^{-}$, AC$, SO_4^{2-}$), alkali, reaction solvent, hydrothermal time/temperature, template (surfactant), then the shape can be maintained during the second ion-exchange process, resulting in the rational design of morphology-controlling NiCo$_2$S$_4$.

The three-step route is: formation of NiCo(OH)$_{2-x}$CO$_3$ $[0\leq x \leq 1]$, calcination of the precursor to obtain NiCo$_2$O$_4$, and converting of NiCo$_2$O$_4$ to NiCo$_2$S$_4$. The third step involves usually with gas-solid reaction by H$_2$S, S, Na$_2$S with the oxide to obtain the NiCo$_2$S$_4$. 

* E-mail: sunmgz@gdut.edu.cn

Received September 13, 2017; accepted October 9, 2017.
Electrochemical applications

Supercapacitor

As one type of the green energy, the outstanding merit of the SCs is the short charging time under high current density with high power density. Many parameters can influence such performance, and the electrode materials are one of the most key issues. NiCoO₂-based materials have been widely explored as the electrode materials for SCs for their excellent performance.\(^{[19,20]}\) When we change O of NiCoO₂ to S, the NiCoS₄ materials could be obtained with many characteristics: a flexible structure making easier for electrons transportation, high electric conductivity of 100 times than that of NiCoO₂. Such characteristics make NiCoS₄ possess remarkable specific capacitances. Up to now, nearly 2/3 of the published papers on NiCoS₄ are focused on the field of SCs. As pseudo-capacitance material, the following redox reactions happen during the charge-discharge process:

\[
\begin{align*}
\text{NiS} + \text{OH}^- & \rightleftharpoons \text{NiSOH} + e^- \\
\text{CoS} + \text{OH}^- & \rightleftharpoons \text{CoSOH} + e^- \\
\text{CoSOH} + \text{OH}^- & \rightleftharpoons \text{CoSO} + \text{H}_2\text{O} + e^- 
\end{align*}
\]

Very recently, Huang et al.\(^{[11]}\) published the first review paper on the application of NiCoS₄ in SCs, and they made a brief introduction on the structures and morphologies of the NiCoS₄ materials from 0D, 1D, 2D to 3D. In view of this, we will not discuss the development of NiCoS₄ as electrode materials for SCs in details in this minireview. However, we must make one thing clear: NiCoS₄ is a kind of important electrode material possessing potential application in the area of SCs.

Li-ion batteries

In the past decades, intense research efforts have been made in the field of LIBs because of the outstanding merits (high energy and power densities) of LIBs as portable electronic devices.\(^{[21]}\) Owing to the lower cost and higher theoretical capacities, the transition metal disulfides are regarded as the promising electrode materials for LIBs.\(^{[22,23]}\) Recently, with the excellent high conductivity of 1.25 \times 10^4 \text{ S} \cdot \text{m}^{-1}, the bimetallic NiCoS₄ is emerging as the new candidate for the electrode material. When used anode material for LIBs, it is believed that the following reactions are involved:\(^{[24]}\)

\[
\begin{align*}
\text{NiCoS₄} + 8\text{Li}^+ + 8e^- & \rightarrow \text{Ni} + 2\text{Co} + 4\text{LiS} \\
\text{Ni} + 4\text{Li}_2\text{S} & \rightleftharpoons \text{NiS} + 2\text{Li} \\
\text{Co} + \text{Li}_2\text{S} & \rightleftharpoons \text{CoS} + 2\text{Li}
\end{align*}
\]

Yu et al.\(^{[24]}\) claimed that they were the first to report NiCoS₄ as an anode for LIBs, and the material demonstrated high specific capacity (1296 mA h g⁻¹) and extraordinary cycling stability (100% retention for 100 charge-discharge cycle). In fact, a little earlier than this paper, Hu et al.\(^{[25]}\) synthesized NiCoS₄ grown on carbon cloth as an anode for LIBs, and the hybrid material delivered high specific capacity (1275 mA h g⁻¹) and excellent rate performance. At a current density of 1 A g⁻¹, for 100 charge-discharge cycle, the retention is 89.2%. At about the same time, Jin et al.\(^{[13]}\) fabricated hierarchical NiCoS₄ hollow spheres, of which possessed a specific capacity of 696 mA h g⁻¹ for 100 cycles (0.2 A g⁻¹). Liu et al.\(^{[26]}\) prepared hierarchical nanostructured hybrids composed by NiCoS₄ nanosheets and nitrogen-doped graphene/carbon nanotube networks, and the composite material displayed high initial charge capacity of 1225.4 mA h g⁻¹ (0.2 A g⁻¹). Recently, Xu et al.\(^{[27]}\) reported NiCoS₄/NiCoS₄ nanoparticles anchored in 3D graphene aerogel, and the material has a superlong cycling stability of 620 mA h g⁻¹ for 800 cycles (1 A g⁻¹).

Dye sensitized solar cells (DSSCs)

DSSCs have attracted increasing attention for the next-generation photovoltaic devices, possessing such merits as low-cost, easy preparation, transparency, and high power conversion efficiency.\(^{[26,50]}\) The counter electrode (CE) is one of the three key components of the DSSCs. The Pt-free CE materials are one of the hot research topics. Binary metal sulfides such as CoS, NiS, MoS, and so on, are considered as good candidate for CE materials. The working principle of DSSCs can be simply shown in Figure 2. For DSSCs, redox between I₂ and I⁻ is very important. The NiCoS₄ material as the catalyst quickens the reaction rapidly.\(^{[21,31]}\)

![Figure 2](image) The working principle of DSSCs.

The papers by Xiao et al.\(^{[16]}\) and Lin et al.\(^{[17]}\) might be the first two reports on the application of NiCoS₄ as CE for DSSCs. In Xiao’s paper, they prepared a hollow NiCoS₄ single nanorod as CE and reported an efficiency of 4.2%. Lin et al.\(^{[12]}\) synthesized highly transparent NiCoS₄ thin film as CE and obtained an impressive efficiency of 6.14%, which is comparable to the efficiency of Pt (6.29%). Afterwards, several other studies are reported. Self-supported NiCoS₄ nanoneedles were deposited on fluorine-tin-oxide (FTO) glass as CE for DSSCs,\(^{[13]}\) showing an efficiency of 6.9% (vs. Pt with 7.7% efficiency). Interconnected NiCoS₄ nanosheets\(^{[28]}\) exhibited higher power conversion efficiency of 7.22% (vs. NiCoS₄ thin film) after 800 cycles (0.2 A g⁻¹).
Co-dation of NiCo-LDH, and the materials exhibited an onset overpotential of 7.98% (vs. Pt with 8.01% efficiency). Based on the above reports, NiCoS$_4$ shows better performance. Murugan et al.[34] developed NiCoS$_4$/graphene nanohybrid with a high power conversion efficiency of 7.98% (vs. Pt with 8.01% efficiency). Dendrite structured NiCo$_2$S$_4$nanorods showed better performance than Pt with 6.87% efficiency). Dendrite structured NiCo$_2$S$_4$ nanorods were prepared and used as CE for DSSCs,[35] of which NiCoS$_4$ showed better performance. Shanmugam et al.[36] tested the HER activity. The result showed that the nanowire produced 100 mA cm$^{-2}$ at an overpotential of 305 mV. Li et al.[37] constructed NiCoS$_4$ nanowires over 3D graphdiyne foam, and the catalyst exhibits an onset overpotential of only 112 mV with excellent durability for 80 h without negligible loss. Using Ni foam as the current carrier, Jin et al.[38] synthesized NiCo$_2$S$_4$ nanoflakes by sulfidation of NiCo-LDH, and the materials exhibited an onset overpotential of 17 mV, the overpotential at current density of 10 mA cm$^{-2}$ is 65 mV. Shanmugam et al.[39] loaded directly NiCoS$_4$ nanowires on Ni foam, and the catalyst delivered a current density of 10 mA cm$^{-2}$ at overpotentials of 210 m. Using the same current carrier, the NiCoS$_4$@NiFe LDH was applied as the HER catalyst, and the low overpotential of 200 mV was required at the current density of 10 mA cm$^{-2}$. When used as the catalyst for HER, the electrolyte can be alkaline (KOH) or acidic (H$_2$SO$_4$) solution, and the corresponding mechanism is different. For the HER in alkaline media, the following reaction are involved:[39,40]

$$\text{M} + \text{H}_2\text{O} + e^- \rightarrow \text{M-ads} + \text{OH}^- + \text{H}_2$$

and/or the chemical desorption

$$\text{2M-ads} \rightarrow \text{2M} + \text{H}_2$$

where M is the metal atom, and M$_{\text{ads}}$ stands for H adsorbed at the active site of catalyst. However, the HER mechanism in acidic solution involves:[41]

$$\text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_2\text{ads} + \text{H}_2\text{O} (\text{Volmer reaction})$$

$$\text{H}_2\text{ads} + \text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O} (\text{Heyrovsky reaction})$$

$$\text{Or H}_2\text{ads} + \text{H}_2\text{ads} \rightarrow \text{H}_2 (\text{Tafel reaction})$$

Based on the above result, we think that the NiCoS$_4$ based materials are one of the most suitable catalysts for HER with exceptional stability. However, the research is limited, and it needs further research.

### Table 2 Photovoltaic characteristics of DSSCs with NiCoS$_4$ as counter electrodes

| Sample               | $J_{oc}$ (mA·cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | $\eta$ (%) | Ref.  |
|----------------------|--------------------------|--------------|--------|------------|-------|
| NiCoS$_4$ nanorod    | 11.94                    | 0.55         | 48.9   | 3.76       | [16]  |
| NiCoS$_4$ film       | 14.11                    | 0.72         | 60     | 6.1        | [12]  |
| NiCoS$_4$ nanoneedle | 13.38                    | 0.76         | 63.2   | 6.9        | [15]  |
| NiCoS$_4$ nanosheets | 18.37                    | 0.67         | 58.66  | 7.22       | [31]  |
| Dendrite structured  |                          |              |        |            |       |
| NiCoS$_4$S$_2$       | 13.6                     | 0.758        | 68.1   | 7.03       | [9]   |
| NiCoS$_4$/NiS        | 17.7                     | 0.744        | 67     | 8.8        | [32]  |
| NiCoS$_4$/particle   | 17.17                    | 0.69         | 63     | 7.43       | [33]  |
| NiCoS$_4$/graphene   | 15.62                    | 0.72         | 70.5   | 7.98       | [34]  |

### Hydrogen evolution reaction (HER)

Hydrogen is a clean resource without any pollution, and electrochemical water splitting is the most efficient method to produce hydrogen, during which process requires catalyst for cathodic HER. Pt related materials are the most effective catalyst. To replace the noble metal Pt, many other low-cost catalyst have been widely researched, and transition metal dichalcogenides behaved promising activity and stability.[21] Similarly, NiCoS$_4$ is reported to be a kind of effective catalyst for HER (Table 3). Recently, Lu et al.[35] prepared NiCoS$_4$ nanowires on carbon cloth by toptactic conversion of NiCo$_2$O$_4$ and tested the HER activity. The result showed that the nanowire produced 100 mA cm$^{-2}$ at an overpotential of 305 mV. Li et al.[36] constructed NiCoS$_4$ nanowires over 3D graphdiyne foam, and the catalyst exhibits an onset overpotential of only 112 mV with excellent durability for 80 h without negligible loss. Using Ni foam as the current carrier, Jin et al.[38] synthesized NiCo$_2$S$_4$ nanoflakes by sulfidation of NiCo-LDH, and the materials exhibited an onset overpotential of 17 mV, the overpotential at current density of 10 mA cm$^{-2}$ is 65 mV. Shannagam et al.[39] loaded directly NiCoS$_4$ nanowires on Ni foam, and the catalyst delivered a current density of 10 mA cm$^{-2}$ at overpotentials of 210 m. Using the same current carrier, the NiCoS$_4$@NiFe LDH was applied as the HER catalyst, and the low overpotential of 200 mV was required at the current density of 10 mA cm$^{-2}$. When used as the catalyst for HER, the electrolyte can be alkaline (KOH) or acidic (H$_2$SO$_4$) solution, and the corresponding mechanism is different. For the HER in alkaline media, the following reaction are involved:[39,40]

$$\text{M} + \text{H}_2\text{O} + e^- \rightarrow \text{M-ads} + \text{OH}^- + \text{H}_2$$

The electrochemical hydrogen desorption

$$\text{M-ads} + \text{H}_2\text{O} + e^- \rightarrow \text{M} + \text{H}_2 + \text{OH}^-$$

### Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)

ORR and OER are two important oxygen-related reactions that are involved in the metal-air batteries and fuel cells.[41] During such process, sufficient catalysts are needed to have a high electrocatalytic activity. Transition metal chalcogenides are regarded as one of the effective and low cost catalysts. Among them, bimetallic NiCoS$_4$ have been reported to perform excellent ORR and OER activities. For example, the hybrid of NiCoS$_4$/graphene was used firstly as a bifunctional electrocatalyst for ORR and OER.[13] They could be converted to metal oxides/hydroxides which itself are the true active center of the OER as the following equations showing:[38]
M(III)OOH + OH⁻ → M(IV)O(OH)_2⁺ + e⁻

M(IV)O(OH)_2⁺ + OH⁻ → [M(IV)O]⁺ + O₂ + 2H₂O + 2e⁻

[M(III)O]⁺ + OH⁻ → M(III)OOH

Thus, Jin[68] suggested that the metal chalcogenides should be named as the pre-catalyst for OER.

**Strategies to improve the performance**

The electrochemical performance of the NiCoSₓ materials can be affected by many parameters: morphology, size, structure/architecture, composition, etc. Thus we can tune its activity by controlling the morphology, structure, composition and current carrier.

**Morphology**

The shape/structure has great effect on the electrochemical performance because different shape might endow the material with various surface area, pore size distribution, defects, and charge resistance. The above properties can influence the electrolyte/electrode contact area, the electrolyte flowing and ion transportation, the reaction active sites, and finally affect the performance. Therefore, a great deal of NiCoSₓ with various morphology have been prepared.[1] Among numerous shape, the hollow structured NiCoSₓ is worth of enough attention because of such features as distinguishable interior voids, large surface area, and the reduced transport route. In this area, Lou group did brilliant work.[46] However, the systemic research of the morphology effect of NiCoSₓ in the same or similar reaction system is still rare except that reported by Hu[40] and Zhang et al.[51]

**Structure**

The combination of NiCoSₓ with other materials to construct hierarchical architectures can produce rich pore (micro or meso) and induce the so-called synergistic effect among different components,[52] which can finally affect the electrochemical performance. Up to now, various NiCoSₓ-based nanocomposites have been fabricated, such as NiCoSₓ@Ni(OH)₂,[33,34] carbon@NiCoSₓ,[53] NiCoSₓ@CoS₂,[56] NiCoSₓ@CoS,[54] CoS@NiCoSₓ,[57] NiCoSₓ@PPy,[58] MWCNT-COOH@NiCoSₓ,[89] NiCoSₓ@NiS,[60] NiCoSₓ@NiSₓ[61] NiCoSₓ@NiSₓ[62] NiCoSₓ@MnOₓ[63,64] NiCoSₓ@NiMnOₓ[65] NiCoSₓ@NiO,[66] NiCoSₓ@NiFe LDH,[87] NiCoOₓ/CoSₓ[88] NiCoSₓ@NiS,[89] etc.

**Composition**

NiCoSₓ has a spinline structure with AB₂S₄ formula, and its composition can be tuned in certain range. For one aspect, we can change the molar ratio of Ni to Co, for example, CoNiSₓ.[58,76-72] NiₓCoₓS₂.[73-75] For another aspect, the element in A and B position can be changed to other transition metals, such as MnCoSₓ.[59,67] CuCoSₓ,[78,79] FeNiSₓ.[80] Through such modification, the electrochemical performance of the NiCoSₓ related materials can be tuned.

**Current carrier**

The direct incorporation of NiCoSₓ with conductive networks can avoid the use of insulating binder, decrease the contact resistance, favor for the mass/charge transport, thus it will facilitate the electrochemical performance. The current carrier including carbon materials (porous carbon, carbon fiber cloth, carbon fiber paper, graphene,[15,40,63,82] Ni foam,[37,38,83] the carbon offer many advantages: low-cost, flexible, lightweight, richness in pore. The carbon materials can be modified by non-metal element B, N, S, P to further increase the activity as both the substrate and active sites. For porous carbon, the pore size can be controlled by preparation parameters. All those characteristics make the carbon material be good candidates as the current carrier for NiCoSₓ. The Ni foam has better mechanical strength, higher conductivity, relatively superior corrosion stability in alkaline solution. One thing to note is that the surface of Ni foam could be partly passivated when exposed to air for time, and necessary pretreatment should be taken to activate and clean the surface.[84]

**Summary and prospective**

In summary, the studies about NiCoSₓ have witnessed soaring growth especially in the past three years, and the achievements are remarkable in view the wide application of NiCoSₓ in several electrochemistry related fields. However, there is still a great space for the development of the NiCoSₓ-based materials. The preparation method is limited, and innovative manufacturing processes achieving large-scale production should be developed to meet the demand of the industrial applications. Furthermore, the studies are not in-depth, the majority of the papers are experimental observations and explanation, the fundamental understanding of the relationship between structure/performance is still lacking. The theoretical simulation and in-situ observation should be further applied. Finally, it is expected that the NiCoSₓ materials might have potential application in other research area (as a catalyst for heterogeneous reaction).

**Acknowledgement**

This work was financially supported by the Scientific Program of Guangdong Province (Nos. 2014A010106030 and 2016A010104017) and the Foundation of Higher Education of Guangdong Province (No. 2015KTSCX027).

**References**

[1] Gao, Y. P.; Huang, K. I. Chem. Asian J. 2017, 12, 1969.
[2] Xia, C.; Li, P.; Gandi, A. N.; Schwingsenschlögl, U.; Alshareef, H. N. Chem. Mater. 2015, 27, 6482.
[3] Liu, Q.; Jin, J.; Zhang, J. ACS Appl. Mater. Interfaces 2013, 5, 5002.
[4] Sun, M.; Tse, J.; Cheng, G.; Lin, T.; Peng, S.; Deng, F.; Ye, F.; Yu, L. J. Mater. Chem. A 2015, 3, 1730.
[5] Wu, Z.; Pu, X.; Ji, X.; Zhu, Y.; Jiao, F. Electrochim. Acta 2015, 174, 238.
[6] Hou, L.; Jin, J.; Zhang, J.; Rehan, M.; Pang, G.; Zhang, X.; Yuan, C. Mater. Chem. A 2017, 5, 133.
[7] Irshad, A.; Munichandraiah, N. ACS Appl. Mater. Interfaces 2017, 9, 19746.
[8] Chen, W.; Xia, C.; Alshareef, H. N. ACS Nano 2014, 8, 9531.
[9] Anuratha, K. S.; Mohan, S.; Panda, S. K. New J. Chem. 2016, 40, 1785.
[10] Yang, B.; Yu, L.; Yan, H.; Sun, Y.; Liu, Q.; Jin, J.; Song, D.; Hu, S.; Yuan, Y.; Liu, L.; Wang, J. J. Mater. Chem. A 2015, 3, 13308.
[11] Chen, H.; Jiang, Z.; Zhang, L.; Wan, H.; Qi, T.; Xia, D. Nano scale 2013, 5, 8879.
[12] Lin, J.-Y.; Chou, S.-W. Electrochem. Commun. 2013, 37, 11.
[13] Jin, R.; Liu, D.; Liu, C.; Liu, G. RSC Adv. 2015, 5, 84711.
[14] Bezverkhyy, I.; Danot, M.; Afanasiev, P. Inorg. Chem. 2003, 42, 1764.
[15] Banerjee, A.; Upadhyay, K. K.; Bhatnagar, S.; Tathavadekar, M.; Bansode, U.; Agarkar, S.; Ogale, S. B. RSC Adv. 2014, 4, 8289.
[16] Xiao, J.; Zeng, X.; Chen, W.; Xiao, F.; Wang, S. Chem. Commun. 2013, 49, 11734.
[17] Xiao, J.; Wan, L.; Yang, S.; Xiao, F.; Wang, S. Nano Lett. 2014, 14, 831.
[18] Hou, L.; Bao, R.; Chen, Z.; Rehan, M.; Tong, L.; Pang, G.; Yuan, C. Electrochim. Acta 2016, 214, 76.
[19] Dubal, D. P.; Gomez-Romero, P.; Sankapal, B. R.; Holze, R. Nano Energy 2015, 11, 377.
[20] Wu, Z.; Zhu, Y.; Ji, X. J. Mater. Chem. A 2014, 2, 14759.
