Carbon Encapsulated Heazlewoodite Nanoparticles as Highly Efficient and Durable Electrocatalysts for Oxygen Evolution Reactions

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Carbon encapsulation improves the activity and stability of heazlewoodite nanoparticles as oxygen evolution electrocatalysts.

Carbon Encapsulated Heazlewoodite Nanoparticles as Highly Efficient and Durable Electrocatalysts for Oxygen Evolution Reactions

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ABSTRACT

The activity and durability of electrocatalysts are two of the most important factors for their practical applications, such as the electrocatalytic oxygen evolution reactions (OERs) used in water splitting cells and metal-air batteries. In this study, a novel electrocatalyst, few-layered graphitic carbon (~5 atomic layers) encapsulated heazlewoodite (Ni₃S₂@C) nanoparticles (NPs), was purposely designed and experimentally synthesised *via* one-step solid phase pyrolysis method. In the OER test, the Ni₃S₂@C catalyst exhibited an overpotential of 298 mV at current density of 10 mA cm⁻², Tafel slope of 51.3 mV dec⁻¹, and charge transfer resistance of 22.0 Ω, which are better than those of benchmark RuO₂ and most other nickel sulfide-based catalysts reported to date. The improved performance can be ascribed to the high electronic conductivity of graphitic carbon encapsulating layers. Moreover, the encapsulation of graphitic carbon layers provides superb stability without any noticeable oxidation or depletion of Ni₃S₂ NPs within the nanocomposite. The strategy introduced in this work can, therefore, benefit the development of highly stable metal sulfide electrocatalysts without sacrificing the electrocatalytic activity for energy conversion and storage applications.

KEYWORDS

heazlewoodite, electrocatalysts, encapsulation, oxygen evolution reaction, pyrolysis, graphitic carbon

1. Introduction

The oxygen evolution reaction (OER) is recognised as a key half reaction in many electrochemical applications and devices such as solar water

splitting [1], water electrolysis cells [2] and recently, metal-air batteries as a charging reaction [3]. However, the thermodynamically unfavourable and kinetically sluggish OER process requires precious

metal-based catalysts, e.g. RuO₂ and IrO₂, to reduce the overpotential and thereby achieve a current density of 10 mA cm⁻², the metric relevant to solar fuel synthesis [4-7]. But the elemental scarcity and high-cost of such noble metal-based electrocatalysts considerably impede the widespread utilisation of these catalysts. Therefore, the development of highly efficient and earth-abundant electrocatalysts for OERs is of paramount significance in designing efficient and affordable energy conversion and storage devices.

In particular, transition metal sulfides have attracted considerable attention as a promising but less investigated class of OER electrocatalysts [8-10]. The Ni metal rich heazlewoodite (Ni₃S₂) has recently shown desired electrocatalytic behaviour for either oxygen reduction reactions (ORRs) [11], hydrogen evolution reactions (HERs) [12, 13] or OERs [14-17]. However, most transition metal sulfides experience serious oxidation at the high anodic potential required for OER catalysis [8, 18-21]. This unavoidable electrochemical phenomenon hinders the inherent OER activity evaluation and it can also affect the long-term electrocatalytic stability of the catalysts.

One feasible way of minimising the possibility of such oxidation processes, while maintaining reasonable electrocatalytic activity, is to encapsulate the metal sulfide nanoparticles (NPs) with an ultrathin layer of foreign substances. Recently, this strategy has been demonstrated to be potentially advantageous in maintaining the parent structural and chemical integrity of the metal based materials in many electrochemical processes [22-27]. And graphitic carbon is one of the best candidates to achieve this goal as it possesses high electronic conductivity and considerable electrochemical inertness [28]. Moreover, Bao and his co-workers discovered that the interaction between the metallic core and the graphitic shell can change the local work function of the shell, and further improved the electrocatalytic activities [29-33]. A recent report

also suggested the exclusive utility of such hybrid system as an efficient and durable electrocatalyst for OERs [34]. Additionally, the unwanted grain boundaries and defects among the metal sulfide NPs can also be alleviated using this well-designed nanostructure, which can further enhance their electronic conductivity [24, 35]. As such, few-layered graphitic carbon encapsulated transition metal sulfide NPs may be able to deliver a number of physical, chemical and electrical benefits needed for efficient and durable electrocatalysts for OERs.

Herein, for the first time, we report a two-dimensional (2D) carbon nanosheet (CNS) supported few-layered graphitic carbon encapsulated Ni₃S₂ NPs nanocomposite (Ni₃S₂@C/CNS) *via* facile pyrolysis of the solid reaction precursor of nickel-oleate (Ni(OA)₂) and Na₂SO₄ at 700 °C. The overall formation mechanism for the synthesis of the Ni₃S₂@C/CNS nanocomposite was systematically investigated based on the emitted gaseous products during the one-step pyrolysis. We found that during the pyrolysis process, the sulfidation of the Ni precursor by the *in situ* generated H₂S can result in the formation of Ni₃S₂ NPs, which are further encapsulated by a few atomic layers of graphitic carbon through a local chemical vapour deposition (CVD) process. This nanocomposite was applied as an electrocatalyst for OER in 1.0 M KOH electrolyte, showing comparable OER performance and excellent electrocatalytic stability to many transition metal sulfide and precious metal-based electrocatalysts.

2. Experimental

2.1 Chemicals

Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O; ACS reagent, ≥98%), n-Hexane (HPLC grade, ≥95%), and ruthenium (IV) oxide (RuO₂; ≥99.9%) were purchased from Sigma-Aldrich. Sodium oleate

($\text{C}_{18}\text{H}_{33}\text{O}_2\text{Na}$ or NaOA) and sodium sulfate (Na_2SO_4 ; AR grade) were bought from TCI Co. and Univar, respectively. Absolute ethanol was of analytical grade and purchased from Chem-Supply. All chemicals were used as received without any further purification.

2.2 Preparation of $\text{Ni}_3\text{S}_2\text{@C/CNS}$ nanocomposites

First, 3.0 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of Milli-Q[®] water (18 M Ω -cm) followed by the addition of 6.0 mmol NaOA, 30 mL n-hexane and 20 mL ethanol. This mixture was refluxed at 70 °C for 1 h with continuous stirring and cooled down to room temperature. Then, the suspension was transferred into a separatory funnel and the green coloured organic top layer containing $\text{Ni}(\text{OA})_2$ was collected in a beaker (Fig. S-1 in the Electronic Supplementary Material (ESM)). Next, 20 g of Na_2SO_4 was added to the green suspension and dried at room temperature for 48 h. This resultant solid mixture was placed in a planetary zirconia ball miller at room temperature at a speed of 500 rpm for 3 h to prepare a finely ground solid mixture, which was used as a solid reaction precursor for the pyrolysis. After that the greenish coloured solid was pyrolysed from 500 to 900 °C with a heating ramp of 10 °C min⁻¹ under continuous Ar flow (20 sccm) and held for 3 h in a tubular furnace. The samples were allowed to cool down naturally to room temperature under Ar flow. At this stage, the pyrolysed object was washed with copious water and filtered through a 0.45 μm nylon membrane. Finally, the nanocomposite, in the form of a black powder, was dried at 60 °C for 24 h in air and denoted as $\text{Ni}_3\text{S}_2\text{@C/CNS}$. A similar method was followed to prepare the CNS sample at 700 °C without any Ni precursor. Pure Ni_3S_2 was synthesised according to the literature reported elsewhere [36] and calcined at 700 °C under Ar atmosphere. This calcined Ni_3S_2 sample was mixed with the CNS at a weight percentage of 46.2% (denoted as $\text{Ni}_3\text{S}_2/\text{CNS}$).

2.3 Structural characterisations

The bulk crystal structures of the samples were characterised by powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer, equipped with a graphite monochromator) and Raman spectroscopic (Renishaw 100, 632.8 nm He-Ne laser) techniques. A scanning electron microscope (SEM, JSM-7001F) and transmission electron microscope (TEM, Philips Tecnai F20) equipped with an Oxford energy-dispersive X-ray spectroscopy (EDS) unit were used to characterise the surface morphology and nanostructural information. The Brunauer-Emmett-Teller (BET) surface area of the prepared material was estimated through nitrogen adsorption-desorption isotherm in Quantachrome Autosorb-1 equipment. The surface chemical composition and the chemical states of the species in the samples were analysed by X-ray photoelectron spectroscopic (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyser) technique. The thermal decomposition processes of the solid reaction precursor were thoroughly analysed by monitoring the real-time emitted gases (H_2O , CO, H_2S and CO_2) during the pyrolysis from 100 to 900 °C with a heating ramp rate of 10 °C min⁻¹ in an inert (Ar) atmosphere with TG/DSC (TG/DSC, Netzsch STA 449F3) and online mass spectrometer (MS, OmniStar GSD 320).

2.4 Electrochemical characterisations

A homogeneous ink was first prepared by dispersing 4.0 mg of catalyst powder in 1 mL of a solvent mixture of Nafion (5%), absolute ethanol and Milli-Q[®] water with a volume ratio of 1:1:8, followed by continuous ultra-sonication for 1 h. A 12.0 μL (loading: 0.24 mg cm⁻²) aliquot of catalyst ink was drop casted on a clean rotating disk electrode (RDE) and dried in air at room temperature. The OER activities of the catalysts were measured in a standard three-electrode system, where the catalyst loaded RDE, an Hg/HgO (1.0 M

NaOH) electrode and platinum mesh acted as the working, reference and counter electrodes, respectively. A potentiostat (CHI 760D, CH Instruments, USA) was utilised to record the electrochemical responses. The measured current density was normalised to the geometric area of the RDE (0.196 cm²). The polarisation curves and Tafel plots were measured at scan rates of 5 and 1 mV s⁻¹, respectively. All potentials displayed in this work were converted to the reversible hydrogen electrode (RHE) scale with 95% *iR*-compensation using the equation $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098 - 95\% iR_s$, where pH = 14 in 1.0 M KOH electrolyte and R_s stands for the Ohmic resistance of the solution (3-5 Ω). Electrochemical impedance spectroscopic (EIS) measurements were conducted under the same experimental configuration at frequencies ranging from 10⁵ to 10⁻¹ Hz with the overpotential of 300 mV and applied potential amplitude was 5 mV. The electrocatalytic stability was tested using the chronopotentiometry (CP) technique at the current density of 10 mA cm⁻² for 12 h.

3 Results and discussion

Synthesis and structural characteristics

The one-step solid phase synthesis procedure for the concurrent growth of Ni₃S₂@C/CNS nanocomposite is schematically illustrated in Fig. 1 (see the experimental section for details). The Ni₃S₂@C/CNS nanocomposites were prepared by the concurrent sulfidation and carbonisation of the solid reaction precursor of Ni(OA)₂ and Na₂SO₄ at 700 °C under Ar atmosphere (Fig. S-1 in the ESM).

Figure 1 Schematic illustration for the synthesis procedure of Ni₃S₂@C/CNS nanocomposite.

Fig. 2(a) shows the XRD pattern of the sample prepared at 700 °C with obvious phase peaks at $2\theta = 21.7, 31.1, 37.7, 44.4, 49.8,$ and 55.1° corresponding to the (101), (110), (003), (202), (113) and (122) reflection planes of Ni₃S₂ crystal structure (JCPDS 44-1418), respectively. No obvious diffraction peaks for the CNS were observed; which means that the majority of the carbon nanostructures are in the distorted graphitic form. The distorted graphitic form of CNS can be further evidenced by two distinct Raman peaks at 1349.7 and 1600.6 cm⁻¹ (Fig. 2(b)), corresponding to the D and G-bands, respectively [37-39]. In addition, the weak signals within the range of 200-500 cm⁻¹ are consistent with the Raman spectra reported for Ni₃S₂ [40, 41]. These XRD and Raman characterisation results confirm that the bulk chemical structure of the Ni₃S₂@C/CNS nanocomposite is composed of crystalline Ni₃S₂ and distorted graphitic carbon.

Figure 2 (a) XRD pattern and (b) Raman spectra of the Ni₃S₂@C/CNS nanocomposite.

The surface morphology and nanostructural properties of the Ni₃S₂@C/CNS nanocomposite were thoroughly characterised using SEM, TEM and EDS techniques. The SEM images (Figs. 3(a) and 3(b)) show a random arrangement of Ni₃S₂ NPs and CNS, where the Ni₃S₂ NPs are dispersed throughout the nanocomposite, as indicated in Fig. 3b. The composites prepared over 700 °C were observed to be large chunks (Fig. S-2 in the ESM) and may not be beneficial for OER catalysis. Additionally, the BET surface area of Ni₃S₂@C/CNS sample was estimated to be 33.34 m² g⁻¹ (Fig. S-3 in the ESM). In the TEM image (Fig. 3(c)), the majorities of Ni₃S₂

NPs are observed to be within the size of 20-30 nm and are nested on the ultrathin (~10 nm) 2D CNS matrix (Fig. S-4 in the ESM).

Figure 3 (a, b) SEM images, (c) TEM image, (d) HRTEM image, (e) dark-field TEM, (f) EDS mapping of Ni, S, C elements and their corresponding overlay distribution and (g) the EDS line profile of $\text{Ni}_3\text{S}_2@\text{C}$ nanoparticle. The broken yellow circles and pink arrows in (b) indicate the $\text{Ni}_3\text{S}_2@\text{C}$ NPs and CNS, respectively. The insert in (g) shows the elemental distribution corresponding to the line drawn over the $\text{Ni}_3\text{S}_2@\text{C}$ nanoparticle.

The high resolution TEM (HRTEM) images clearly show the encapsulation of graphitic carbon layers on Ni_3S_2 NPs (Fig. 3(d)). The lattice fringes of 3.40 and 4.08 Å can be attributed to the reflection plane of (002) in graphitic carbon and (101) in crystalline Ni_3S_2 , respectively. This suggests that ~5

atomic layers of graphitic carbon with the thickness of ~1.8 nm have successfully encapsulated the Ni_3S_2 NPs. This thin layer graphitic carbon might provide a geometric confinement to Ni_3S_2 NPs leading to a close interface contact and can spontaneously prohibit the surface oxidation of Ni_3S_2 with maintaining a promising electrochemical OER activity [42-44].

The EDS measurements were also conducted to visualise the elemental distribution within the entire nanocomposite. As evidenced by Figs. 3(e) and 3(f), the NPs are mainly composed of Ni and S, where the C signals are relatively weak on the NPs, implying the low concentration of C there. However, the EDS line-profile in Fig. 3(g) clearly shows relatively higher concentration of elemental C (yellow line) at the edges of the NP, certifying successfully encapsulated Ni_3S_2 NPs by a few-layered graphitic carbon *via* this one-step pyrolysis method. Moreover, the EDS pattern (Fig. S-5 in the ESM) obtained from the fields of the $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ nanocomposite indicates an average Ni/S atomic composition of 3:2.

Figure 4 (a) XPS survey spectra, high resolution (b) Ni 2p, (c) S 2p and (d) C 1s spectra of $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ nanocomposite.

The surface chemical states of the as prepared $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ nanocomposite were examined by

XPS. As shown in Fig. 4(a), Ni, S, O and C elements are dominant in the nanocomposite. The oxidation states of Ni were investigated by the deconvolution of high resolution Ni 2p spectra (Fig. 4(b)). The Ni 2p_{3/2} and Ni 2p_{1/2} doublet peaks centred at 855.4 and 873.0 eV accompanied by their respective satellite peaks (denoted as "Sat.") with the split spin-orbit of ~17.6 eV and a characteristic peak at 852.4 eV confirm the formation of Ni₃S₂ crystals, which are consistent with the literature [14, 45, 46]. In Fig. 4(c), two main characteristic peaks for S²⁻ species at 161.6 and 162.7 eV were observed, which are related to the S 2p_{3/2} and S 2p_{1/2} states [47, 48]. Along with the XPS signals for S²⁻ states, the S_n²⁻ and S⁶⁺ states were also observed [38, 48-51]. The C 1s XPS spectrum (Fig. 4(d)) reveals the existence of C-C/C=C, C-O, C=O and O-C=O bonds in the nanocomposite. Apart from the graphitic bonds, other functional groups of CNS may benefit its binding with Ni₃S₂@C NPs, leading to an improved interfacial connection between the Ni₃S₂@C and CNS, beneficial for electrocatalytic OER applications.

It has been speculated that the amount of Ni₃S₂ in the nanocomposite obtained from the EDS and XPS analysis may be underestimated [31, 52] owing to the few-layered graphitic carbon coatings on Ni₃S₂ NPs. To avoid this discrepancy and to study the thermal stability of the nanocomposite, simultaneous thermogravimetric (TG)/differential scanning calorimetric (DSC) measurements were conducted. The TG/DSC profile (Fig. 5(a)) obtained for the sample burnt from 100 to 900 °C under air at a heating rate of 10 °C min⁻¹ showed an initial weight loss of ~8.6% from 100 to 473 °C, implying the evaporation of adsorbed H₂O and the successive decomposition of labile functional groups (C-O, C=O, O-C=O, etc.) detected in the XPS measurement. However, a further weight loss of ~48.3%, along with a broad exothermic DSC peak at ~570 °C was observed, suggesting the simultaneous oxidation of Ni₃S₂ and carbon to their corresponding oxides (NiO and CO₂). Above 650 °C, a stable TG profile

reflects the formation of stable NiO, as confirmed by the XRD pattern in Fig. 5(b). Based on the final weight of NiO remaining as residue, the original fraction of Ni₃S₂ in the nanocomposite was calculated to be 46.2% by weight.

Figure 5 (a) TG/DSC curves obtained for Ni₃S₂@C/CNS sample in air from 100 to 900 °C; (b) XRD pattern of the materials remaining after burning the Ni₃S₂@C/CNS nanocomposite at 900 °C in air; (c) TG/DSC and (d) MS curves obtained from the pyrolysis of the solid precursor (Ni(OA)₂+Na₂SO₄) under Ar protection from 100 to 900 °C with a heating ramp of 10 °C min⁻¹.

The instantaneous TG/DSC-MS measurements were performed to understand the formation mechanism of Ni₃S₂@C/CNS nanocomposite. According to our previous work [50, 53], the concurrently grown products are heavily dependent on the decomposition characteristics of each existing component in the solid reaction precursor. Also, a certain quantity of thermal energy is essential to trigger each decomposition event and the relevant chemical reactions inside the pyrolysis tube. A synchronous TG/DSC-MS measurement enables us to monitor the TG/DSC profile along with the emitted gaseous products during pyrolysis. The TG/DSC-MS measurement of the solid reaction precursor was performed under the same experimental conditions used for the nanocomposite fabrication. As shown in Fig. 5(c),

the initial major breakthrough started at 293 °C and continued up to 500 °C with a weight loss of ~5.10%, as evidenced by the strong endothermic DSC peak and simultaneous peaked emissions (Fig. 5(d)) of the gaseous products (H₂O, H₂S, CO₂). It suggests that the decomposition of Ni(OA)₂ resulted in the formation of Ni⁰ NPs (Figs. S-2 and S-6 in the ESM) and amorphous carbon (Eq. 1). A broad endothermic peak and an obvious weight loss of 0.88% (Fig. 5(c)) from 567 to 760 °C (Fig. 5(d)) may arise from the reduction of Na₂SO₄ (Eq. 2) by carbon to produce Na₂S. Thereafter, the hydrolysis of Na₂S (Eq. 3) leads to the formation of H₂S, as supported by the MS peaked H₂S emission (Fig. 5(d)). After that, H₂S can further sulfidise the Ni⁰ NPs to yield Ni₃S₂ NPs (Eq. 4). Furthermore, the Na₂SO₄ salt not only assisted nanostructure formation on its surface but also provided the desired amount of sulfur sources for the sulfidation of metallic Ni NPs. Based on the aforementioned discussion and corresponding XRD analysis (Fig. S-6 in the ESM), a plausible reaction mechanism is outlined below.

It is noteworthy that the nanostructure obtained in this work is very different from that achieved in our previous work [50] owing to the different pyrolysis mechanism. As shown in Fig. 3d, the carbon used to encapsulate Ni₃S₂ NPs was in the graphitic form, whereas the carbon in the CNS was distorted or partly amorphous. This discriminative nature of carbonisation at this moderately high temperature pyrolysis event may arise from the catalytic graphitisation characteristics of metallic Ni⁰ NPs [54, 55] formed at lower pyrolysis

temperatures (<700 °C) (Fig. S-6 in the ESM). The high carbon diffusion coefficient (2×10⁻¹¹ m² s⁻¹) in metallic Ni [56, 57] can result a local CVD [58] growth of graphitic carbon on Ni₃S₂ NPs. During the simultaneous sulfidation and carbonisation process which took place at 700 °C, carbon atoms are believed to diffuse into the Ni⁰ NPs and are partially displaced by the sulfur atoms sourcing from the *in situ* generated H₂S gas to form Ni₃S₂ NPs. Through this displacement, carbon atoms may get precipitated on Ni₃S₂ NPs surface which in turn led to the formation of few-layered graphitic carbon encapsulating layer and thereby the final Ni₃S₂@C/CNS nanocomposite.

Electrocatalytic performances

The electrocatalytic OER performances of the electrocatalysts were examined in 1.0 M KOH electrolyte using a standard three-electrode system (see the experimental section for details). To identify the function of few-layered graphitic carbon on Ni₃S₂ NPs, two control samples including Ni₃S₂/CNS, Ni₃S₂ (Fig. S-7 in the ESM) were also tested under identical conditions on a glassy carbon electrode (GCE).

As it evident from the polarisation curves (Fig. 6(a)), the CNS is not active to the catalytic OERs. Also, the products obtained below or over 700 °C showed poor electrocatalytic performances, which can be ascribed to the severely destroyed nanostructures and various crystal phases (Figs. S-2, S-6 and S-8 in the ESM). Interestingly, the product synthesised at 700 °C (Ni₃S₂@C/CNS) exhibits the earliest onset potential of ≈1.45 V (vs. RHE), which is fairly close to that of the benchmark RuO₂ and slightly better than those of Ni₃S₂/CNS and Ni₃S₂ catalysts. However, the overpotential required to reach the current density of 10 mA cm⁻² is 298 mV for the Ni₃S₂@C/CNS electrode, which is 10, 26 and 37 mV lower than those of RuO₂, Ni₃S₂/CNS and Ni₃S₂, respectively. The smallest overpotential of Ni₃S₂@C/CNS among all considered catalysts

reveals that the encapsulation of few-layered graphitic carbon can improve the OER performance. It is also worthwhile to mention that Ni_3S_2 and $\text{Ni}_3\text{S}_2/\text{CNS}$ samples showed a peak at ~ 1.43 V (see Fig. 6(a)), which can be attributed to the reversible redox reaction of $\text{Ni(II)} \leftrightarrow \text{Ni(III)}$ in alkaline solution [59, 60]. Whereas, a tiny fraction of peak current was observed for $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ sample, meaning the successful protection of Ni_3S_2 NPs due to the few-layered graphitic carbon encapsulation.

Figure 6 (a) Polarisation curves, (b) Tafel plots, (c) Nyquist plots of $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$, $\text{Ni}_3\text{S}_2/\text{CNS}$, Ni_3S_2 and RuO_2 ; (d) cyclic voltammograms of the $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ catalyst at scan rates of 10 to 180 mV s^{-1} ; (e) plots of current densities at 1.225 V vs. scan rates of $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$, $\text{Ni}_3\text{S}_2/\text{CNS}$, Ni_3S_2 and RuO_2 ; (f) chronopotentiometric (CP) plots of the $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$, $\text{Ni}_3\text{S}_2/\text{CNS}$, Ni_3S_2 and RuO_2 catalyst in 1.0 M KOH electrolyte.

To gain insight into the OER kinetics, Tafel plots were constructed as shown in Fig. 6(b). The $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ electrode shows a Tafel slope of 51.3 mV dec^{-1} , which is slightly smaller than that of RuO_2 (52.4 mV dec^{-1}), however, significantly smaller than $\text{Ni}_3\text{S}_2/\text{CNS}$ (65.1 mV dec^{-1}) and Ni_3S_2 (95.1 mV dec^{-1}).

The relatively smaller Tafel slope suggests that the superior OER kinetics of the $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ catalysts.

Typically, the OER kinetics is associated with the charge transfer process, which was further investigated by electrochemical impedance spectroscopy (EIS). As displayed in Fig. 6(c), the charge transfer resistance (R_{ct}) of $\text{Ni}_3\text{S}_2/\text{CNS}$ (46.6 Ω) is 32.4% lower than that of Ni_3S_2 (68.9 Ω) due to the introduction of conductive CNS. After few-layered graphitic carbon encapsulation on Ni_3S_2 NPs, a further improvement (52.8%) on the R_{ct} value is observed for $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ (22.0 Ω) catalyst. Also, the R_{ct} value of $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ is even lower than that of the benchmark RuO_2 catalyst (25.5 Ω). The small charge transfer resistance is consistent with the conclusion through the comparison of Tafel slope values, which can be ascribed to the tight binding between the Ni_3S_2 NPs and graphitic carbon layers, as demonstrated by the HRTEM (see Fig. 3(d)). Obviously, the introduction of carbon encapsulating layer on Ni_3S_2 NPs induces an enhanced catalytic activities, which is consistent with the literature [30, 61] but the identification of the real active sites in this hybrid core-shell heterostructure still remains unclear.

In addition to the kinetic study, the electrochemical active surface area of the catalyst was examined by comparing the electrochemical double-layer capacitance (C_{dl}) under non-Faradaic potential window [62]. The corresponding C_{dl} values of all the electrocatalysts were calculated from the cyclic voltammograms (Figs. 6(d) and S-9 in the ESM) and presented in Fig. 6(e). The highest C_{dl} value of $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ (23.4 mF cm^{-2}) with respect to $\text{Ni}_3\text{S}_2/\text{CNS}$ (6.6 mF cm^{-2}), Ni_3S_2 (4.9 mF cm^{-2}) and RuO_2 (8.8 mF cm^{-2}) indicates the largest amount of electrocatalytic active sites. This is because of the aggregation of Ni_3S_2 NPs can be prohibited by the graphitic carbon layers on NPs during the synthesis, which can, therefore, increase the surface area of the catalyst.

Based on the aforementioned electrochemical measurements, $\text{Ni}_3\text{S}_2\text{@C/CNS}$ shows improved OER activities due to the encapsulation of few graphitic carbon layers. It is worth noting that the performance of this novel $\text{Ni}_3\text{S}_2\text{@C/CNS}$ electrocatalysts is also better than that of many other nickel sulfide catalysts reported to date for OERs (see Table S-1 in the ESM).

Besides the thermodynamic and kinetics assessments, the electrocatalytic OER stability was also tested by chronopotentiometric (CP) measurement at the current density of 10 mA cm^{-2} . As displayed in Fig. 6(f), $\text{Ni}_3\text{S}_2\text{@C/CNS}$ showed impressive electrocatalytic durability in 1.0 M KOH electrolyte where the operating potential remained close to $\approx 1.537 \text{ V}$ (vs. RHE) for 12 h of testing period. On the other hand, $\text{Ni}_3\text{S}_2\text{/CNS}$ and Ni_3S_2 electrodes were found to be gradually activated with an obvious trip to a decreased overpotential after 10 h of OER test, which is possibly related to the electrochemical conversion of Ni_3S_2 to its corresponding oxyhydroxide or vice versa [8, 18, 19, 63]. In contrast, the electrocatalytic performance of RuO_2 was recorded to get decreased rapidly with time. Therefore, the steady state catalytic behaviour of $\text{Ni}_3\text{S}_2\text{@C/CNS}$ catalyst in the CP test indicates the spontaneous protection of Ni_3S_2 NPs due to the few-layered graphitic carbon encapsulation.

Figure 7 XPS spectra of (a) Ni 2p and (b) S 2p of $\text{Ni}_3\text{S}_2\text{@C/CNS}$, $\text{Ni}_3\text{S}_2\text{/CNS}$ and Ni_3S_2 after 12 h of OER test in 1.0 M KOH .

To identify the role of carbon encapsulation in enhancing the electrocatalytic OER stability, XPS measurements were conducted on the sample used

for the 12 h OER durability test. As evidenced by Fig. 7(a), the characteristic peak of Ni_3S_2 (852.4 eV) is retained for $\text{Ni}_3\text{S}_2\text{@C/CNS}$, whereas this XPS signals are disappeared for both $\text{Ni}_3\text{S}_2\text{/CNS}$ and Ni_3S_2 samples. This scenario indicates the unavoidable electrochemical oxidation of Ni_3S_2 to oxyhydroxide or hydrated oxide in the absence of carbon encapsulation [14, 46].

Similar phenomenon was also observed from the S 2p XPS spectra as presented in Fig. 7(b). The sulfur species are found to be depleted for $\text{Ni}_3\text{S}_2\text{/CNS}$ and Ni_3S_2 samples. However, the S 2p spectrum for $\text{Ni}_3\text{S}_2\text{@C/CNS}$ sample displayed almost unchanged XPS signal after the 12 h OER durability test, which suggests a negligible change in the sulfur chemical states. Therefore, it confirms that the encapsulation of few-layered graphitic carbon on Ni_3S_2 NPs has successfully secured the parent chemical structure and ensured an excellent electrocatalytic OER stability, as suggested by the CP measurements (Fig. 6(f)).

4 Conclusions

In summary, the few-layered graphitic carbon encapsulated heazlewoodite nanoparticle catalyst supported on the 2D carbon nanosheet ($\text{Ni}_3\text{S}_2\text{@C/CNS}$) was successfully fabricated using a facile, cheap and one-step solid phase pyrolysis approach. The formation mechanism of $\text{Ni}_3\text{S}_2\text{@C/CNS}$ was comprehensively studied using a combined TG/DSC-MS and XRD analysis, which demonstrates a sequence of chemical reactions occurring during the pyrolysis process along with a local CVD growth of graphitic carbon layer. The electrocatalytic performances reveal the two-fold functions of carbon encapsulation. First, the smaller Tafel slope and charge transfer resistance compared to those of benchmark RuO_2 and control samples suggest that the few-layered graphitic carbon can significantly improve electronic conductivity. Second, the remarkable electrocatalytic durability is achieved by avoiding the electrochemical oxidation of Ni_3S_2 due to the protection of the graphitic carbon layers.

We, therefore, believe that the encapsulation of metal-sulfide NPs by the few-layered conductive and chemically inert graphitic carbon is a feasible and effective way of enhancing the activity and durability of electrocatalysts for OER, which can also be useful to the molecular design of novel nanomaterials involved in energy conversion and storage applications.

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Electronic Supplementary Material

Carbon Encapsulated Heazlewoodite Nanoparticles as Highly Efficient and Durable Electrocatalysts for Oxygen Evolution Reactions

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Fig. S-1 Digital photographs taken at the different stages of $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ nanocomposite fabrication.

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Fig. S-2 SEM images of the samples prepared at (a) 500, (b) 600, (c) 800 and (d) 900 °C under the same experimental conditions.

Fig. S-3 Nitrogen adsorption-desorption isotherm of Ni₃S₂@C/CNS nanocomposite.

Fig. S-4 SEM image of the pristine CNS sample prepared at 700 °C displaying the thickness of ~10 nm.

Fig. S-5 EDS results of the $\text{Ni}_3\text{S}_2@\text{C}/\text{CNS}$ nanocomposite.

Fig. S-6 XRD pattern of the samples prepared at 500, 600, 700, 800 and 900 °C under Ar atmosphere. The peaks with “*” originated from the elemental sulfur species.

Fig. S-7 (a) SEM image and (b) XRD pattern of Ni_3S_2 prepared by the hydrothermal method and calcinated at 700 °C under Ar atmosphere.

Fig. S-8 Polarisation curves of the samples prepared at different pyrolysis temperatures from 500-900 °C.

Fig. S-9 Cyclic voltammograms of (a) $\text{Ni}_3\text{S}_2/\text{CNS}$, (b) Ni_3S_2 and (c) RuO_2 at different scan rates from 10 to 180 mV s^{-1} at the potential window of 1.20-1.25 V (vs. RHE).

Table S1. A partial literature summary of the OER performances of nickel sulfide catalysts tested in 1.0 M KOH electrolyte.

Catalysts	$\eta@10 \text{ mA cm}^{-2}$	Onset potential (V vs. RHE)	Tafel slope (mV dec ⁻¹)	Mass loading (mg cm ⁻²)	Substrate	Reference
Fe _{0.1} -NiS ₂ /Ti	231 ^(a)	~1.40	43	0.8	Ti	[1]
Fe _{11.8%} -Ni ₃ S ₂ /NF	253 ^(a)	~1.45	65	7.9	Ni foam	[2]
Ni ₃ S ₂ /NF	260	~1.35	-	1.6	Ni foam	[3]
Ni₃S₂@C/CNS	298	~1.46	48.2	0.25	GCE	This work
Ni ₃ S ₂ /NF	300	~1.50	51	-	Ni foam	[4]
MoO _x /Ni ₃ S ₂	310 ^(a)	~1.45	50	12	Ni foam	[5]
NiS	320	~1.48	-	0.14	FTO	[6]
NiS	~335 ^(a)	~1.55	89	43	Ni foam	[7]
Ni ₃ S ₂ @Ni	340	~1.50	150	-	Ni foam	[8]
Ni ₉ S ₈	340 ^(b)	~1.50	109.8	11.04	Ni foam	[9]
NiS _x	353	~1.52	56	0.5	GCE	[10]
NiO-NiS/N-C	374	~1.56	64.1	0.2	CFP	[11]
Ni ₃ S ₂ @NC	390	~1.50	196	0.22	GCE	[12]
NiS@N/S-C	417	~1.54	48	0.2	CFP	[13]
NGC@Co ₄ S ₃ /Ni _x S ₆	420 ^(c)	~1.55	37	0.28	GCE	[14]

Corresponding overpotentials at (a) 100, (b) 30 and (c) 22.55 mA cm⁻²

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