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Supercritical Fluid Processing for the Synthesis of NiS₂ Nanostructures as Efficient Electrocatalyst for Electrochemical Oxygen Evolution Reaction⁺

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In this work, synthesis of NiS₂ nanostructures using a simple and onestep environmentally benign supercritical fluid processing within 60 min reaction time has been demonstrated. The structural and morphological characterizations have been performed to confirm the as synthesized product was cubic NiS₂ nanostructures. Interestingly, the as prepared NiS₂ nanostructures exhibit superior electrocatalytic activity towards the oxygen evolution reaction with a small overpotential of 264 mV vs. RHE at 10 mA cm⁻² and a Tafel slope of 105 mV dec⁻¹. Remarkably, the observed catalytic activity of NiS₂ nanostructures are very close resemblance to the benchmark IrO₂ catalyst where IrO₂ shows the overpotential of 260 mV with a Tafel slope of 95 mV dec⁻¹. Thus, the as-synthesized NiS₂ nanostructures can be considered as promising material for the replacement of noble metal based IrO₂ catalyst.

Introduction

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Electrochemical splitting of water $(H_2O \rightarrow H_2 + 1/2O_2)$ into molecular hydrogen (H_2) and oxygen (O_2) is an effective, ecofriendly, earth abundant and low cost renewable energy approaches. It can be considered as clean energy process since there is no greenhouse gases evolution that damage the environment as like conventional fossil fuels. The overall water splitting reaction was mainly hampered by anodic four electron/proton transfer oxygen evolution reaction (OER) compared to the two electron/proton transfer cathodic hydrogen evolution reaction (HER). Hence, the anodic OER is a rate-limiting and energy intensive process that requires large overpotential and more energy consumption.^{1,2} In order to minimize the energy consumption/overpotential and simultaneously

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enhance the efficiency of water splitting process, catalyst is needed to accelerate the rate of reaction.² Precious metals and their oxides (Pt, IrO₂ and RuO₂) were used as efficient OER catalysts and they exhibits a lower overpotential (η). However, it was limited to large scale deployment because of their low earth abundance, high cost and instability under long-term OER condition in acid or alkaline medium.³⁻⁶ Numerous efforts have been devoted to develop highly active OER catalysts with low cost and earth abundant. Hence, the non-noble metal based transition metal oxides, hydroxides, oxyhydroxides, phosphides, phosphates, sulphides, selinides, borates and perovskites have received much attention and extensively explored due to their good catalytic activity as well as stability in wide pH range.⁷⁻²⁵

Generally, Ni based compounds were reported as the attractive OER catalysts due to the active (γ -NiOOH to β -NiOOH) intermediates formation in alkaline medium,²⁶ which are mainly responsible for an enhanced OER. Among the various Ni based compounds, nickel sulphides have aroused much interest due to its multifarious applications in various fields and it has the more number of crystalline phases such as α -NiS, β -NiS, NiS₂, Ni₃S₄, β -Ni₃S₂, Ni₇S₆ and Ni₉S₈.²⁷ It is important to note that coexistence of nickel sulphides with different crystalline phases and morphologies is common during the conventional synthesis. Thus, the phase pure preparation of nickel sulphide with uniform morphology is highly warranted for desired applications. Recently, Zhou et.al. reported the fabrication of Ni₃S₂ nanorods/Ni foam composite by hydrothermal method and they explored these composite electrode material for electrocatalytic OER with a low overpotential of ~157 mV.²⁸ A very few attempts have been made to synthesis the cubic NiS₂ nanostructures for supercapacitor, HER, and oxygen reduction reaction applications.²⁹⁻³³ Indeed, there are no attempts have been made to synthesize the NiS₂ nanostructures by supercritical fluid (SCF) processing and also its application in electrocatalytic OER is not known in literature. Here, the NiS₂ nanostructures were prepared using the environmentally benign SCF processing and exploited for

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electrochemical OER in alkaline medium. Recently, SCF assisted synthesis of inorganic nanomaterials has been considered as the promising route for diverse applications.³⁴ SCF reaction medium was created by increasing the temperature and pressure of the solvents above their critical points, where a single homogenous phase was formed. Thus, the fluid has both vapour and liquid properties such as gas-like diffusivity, liquid-like solvent properties along with low viscosity.³⁵ Remarkably, the particle size distribution and morphology of the nanomaterials can be tuned by varying the parameters such as temperature, pressure and fluid medium. Since the physical properties of the fluids such as density, viscosity and dielectric constant can be altered with temperature and pressure. In addition, the surface tension of the fluid was completely vanished in the SCF condition which is an essential parameter to control the surface and interface chemistry of the nanostructures. Recently, the SCF method has been extended for the preparation of high quality few layer 2D inorganic nanomaterials from their bulk materials in a short reaction time.³⁶⁻⁴⁰

In this work, the ethanol-toluene mixture has been utilized as SCF for the synthesis of NiS₂ nanostructures in a short reaction time of 60 min. The as-synthesized NiS₂ nanostructures showed the superior OER catalytic activity with a small overpotential of 264 mV vs. RHE at 10 mA cm⁻² and a Tafel slope of 105 mV dec⁻¹.

Experimental section

Synthesis of NiS₂ nanostructures:

NiS₂ nanostructures were synthesized using one-pot SCF processing. In a typical synthesis, 1 mmol of nickel (II) nitrate hexahydrate and 2 mmol of commercial sulphur powder was taken and dissolved in 12.5 mL ethanol and 12.5 mL toluene solution, respectively. The solutions were mixed together and ultrasonicated for 15 min. Then, the resulted homogenous solution mixture was poured into a 35 mL supercritical reactor and placed in a preheated vertical tubular furnace at 400 °C for 60 min. The reactor was quenched in an ice cold water bath and the obtained black colour precipitate of NiS₂ was collected by repeated washing with ethanol-water mixture using centrifugation and then dried in a hot air oven at 70 °C for 6 h. For comparison, NiS₂ nanostructures were also prepared by solvothermal method using the same precursor solutions in a 50 mL Teflon lined autoclave reactor at 180 °C for 24 h. The obtained NiS₂ nanostructures by SCF and solvothermal methods are designated as NiS₂ SCF and NiS₂ Sol in the further results and discussion, respectively.

Structural characterizations:

The crystalline nature of as-synthesized NiS₂ product was confirmed by powder X-ray diffraction pattern using BRUKER D8 ADVANCE X-ray Diffractometer with Cu K α radiation (α = 1.5418 Å). The XRD was recorded from 2 θ = 10 to 80° in steps of 0.02° and a count time of 0.2 s. The formation of NiS₂ product was further confirmed by Raman spectroscopy using RENISHAW Invia laser Raman microscope system with He-Ne laser having a

wavelength of 633 nm. The morphological studies icof or has synthesized NiS₂ product was evaluated Osing 1960 and 1960

Electrochemical measurements

The electrochemical studies were performed using Autolab potentiostat-galvanostat (model PGSTAT-30) electrochemical workstation. OER measurements were carried out using cyclic voltammetric (CV) method in a standard three electrode setup where 1 M KOH solution and Pt wire were served as the electrolyte and counter electrode, respectively. Further, saturated calomel electrode and NiS₂ catalyst modified carbon paper (CP) were used as the reference electrode and working electrode, respectively. The catalyst ink was prepared by dispersion of 2 mg of catalyst in 450 µL of water and 50 µL of Nafion (5 wt% isopropanol) solution by 30 min ultrasonication. The working electrode was prepared by drop casting the above catalyst ink (0.3 mg loading) in the area of 1 cm² of CP substrate. CV measurements were conducted at the static condition of working electrode. Whereas the electrolyte solution was stirred at constant rotation. The linear portion of anodic curve in CV was taken as linear sweep and mentioned as a linear sweeping voltammetry (LSV). The potentials were calibrated to a reversible hydrogen electrode (RHE) using the relation of E_{RHE} = $E_{Measured} + E_{Ref} + 0.059*pH$. The overpotential (η) was calculated using the following equation: $\eta = E_{Observed} - E_{Equ}$ at the current density of 10 mA cm⁻². Electrochemical impedance spectroscopy (EIS) were measured in the frequency range from 1000 kHz to 10 mHz with an amplitude of 30 mV under the OER condition (300 mV of η) for the charge transfer kinetics.

Results and Discussion

Fig. 1a represents the typical XRD pattern of as-synthesized product by one-pot facile SCF processing and the standard reference pattern of cubic NiS₂ (JCPDS No: 01-089-3058). The observed well-defined diffraction peaks are readily indexed to the cubic NiS₂ phase with lattice parameter of a = 5.67 Å. It is important to mention here that other non-stoichiometric nickel sulphide phases and impurities were not detected in the XRD pattern. It proves that the as-synthesized NiS₂ product is in a single phase with high purity. In addition, the high intense diffraction lines indicate the obtained NiS₂ product is well crystalline in nature even without any thermal heat treatment. XRD pattern for the NiS₂ product obtained by solvothermal method is shown in Fig. S1. It clearly indicated that the significant amount of NiSO₄.H₂O (JCPDS No: 021-0974) impurity coexists with cubic NiS₂ product. These results clearly revealed

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that SCF processing is an effective route for the synthesis of phase pure crystalline nanomaterials in a short reaction time. Raman spectra of as-synthesized NiS₂ SCF product was shown in Fig. 1b. The first two broad peaks was deconvoluted and shown in Fig. S2. The observed peaks in the deconvoluted spectra at 237, 272, 507 and 565 cm⁻¹ are the characteristic peaks of NiS₂ crystals.^{41,42} The other two deconvoluted peaks at 164 and 194 cm⁻¹ are assigned to the other stoichiometric nickel sulphide systems.⁴² In addition, the observed broad peaks around at 710 and 1080 cm⁻¹ revealed the formation of NiO nanoparticles over NiS₂ surface.⁴³ However, these oxide layer was not determined by the XRD due to very thin layer or amorphous NiO.²⁸ It clearly suggests that the surface of NiS₂ nanostructures were oxidized under an air atmosphere or high temperature SCF treatment which is well consistent with XPS analysis.



Fig. 1 (a) XRD pattern and (b) Raman spectra of as synthesized $\ensuremath{\text{NiS}}_2$ SCF nanostructures.

Electron microscopic analysis has been employed to investigate the surface morphology of the as-synthesized sample obtained by SCF processing. Fig. 2 represents the FE-SEM images of NiS₂ sample that is coated over silica substrate. It revealed that the obtained NiS₂ nanostructures have lateral dimensions ranging from 50 to 200 nm.



Fig. 2 (a-d) FE-SEM images of the as synthesized NiS_2 SCF nanostructures.

The formation of NiS₂ nanostructures under SCE condition was further confirmed by HR-TEM analysis (Fig.13)./FRE Nateral size of NiS₂ nanostructures were in good agreement with FE-SEM analysis. The transparent thin nanostructures observed at the high magnification TEM images (Fig. 3c-d & S3). SAED pattern indicated the crystalline nature of NiS₂ under SCF condition which is in good agreement with the XRD observations. The lattice fringes values have been measured and found to be 0.25 nm that corresponds to the (210) plane of cubic phase of NiS₂. To identify the presence of elements in the as synthesized NiS₂ nanostructures, SEM-EDX analysis have been performed and it is presented in Fig. S4. It showed the peak that corresponds to Ni, S and O elements. It revealed that the as synthesized sample comprised of Ni and S with no other impurity.



Fig. 3 (a-e) HR-TEM images of the as synthesized NiS_2 SCF nanostructures and (f) the corresponding SAED pattern.

However, the detected oxygen peak indicates that NiS_2 surface was mildly oxidized in an atmospheric condition and/or SCF condition, which is well consistent with XPS analysis results (Fig. 4). The high resolution Ni 2p spectra shows four peaks in which the prominent peaks at 854.2 and 871.5 eV are attributed to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively.^{44,45} While, the other two weak peaks at 860 and 879 eV can be ascribed to the binding energy values of nickel where it is linked to oxygen species.²⁸ It suggested that NiS₂ nanostructure surfaces were oxidized when it is exposed to atmosphere and/or under high temperature SCF

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treatment. Fig. 4b shows the deconvoluted S 2p spectra, wherein 1:2 intensity ratio of S $2p_{1/2}$ and S $2p_{3/2}$ peaks can be seen at 163.6 and 162.3 eV, respectively.^{46,47} Surprisingly, another broad peak was observed at 166-172 eV is due to the oxidized sulphur species.⁴⁸⁻⁵⁰



Fig. 4 (a) Ni 2p and (b) S 2p high resolution XPS spectra of NiS_2 SCF nanostructures.

Electrocatalytic OER activity of NiS2 SCF nanostructures on CP substrate (NiS₂ SCF-CP) were examined using CV measurements and its activity was compared with NiS₂ sol (NiS₂ Sol-CP), commercially purchased NiO (Sigma Aldrich) (NiO-CP) and benchmark IrO₂ (IrO₂-CP) electrocatalysts. Fig. 5a display the CVs of NiS₂ SCF-CP, NiS₂ Sol-CP and NiO-CP were recorded at a scan rate of 2 mV s⁻¹ in 1 M KOH solution. All the electrocatalysts show a pair of redox peaks around at 1.35 and 1.25 V vs. RHE in the anodic and cathodic direction, respectively. It corresponds to the redox reaction between Ni²⁺ and Ni^{3+} ($Ni^{2+} + OH^- \leftrightarrow NiOOH + e^-$).¹⁶ It is important to mention here that the similar redox peaks were also observed by Chen et.al, where they have synthesized the NiSe2 on Ni foam and studied their catalytic activity towards OER.16 To ensure the extent of adsorption of OH⁻ ions on the surface of different electrocatalysts during the OER, Faradaic active sites have been calculated from the voltammetric charge (q*) based on the eqn 1. The magnitudes of Faradaic active sites reflects the adsorption capacity of OH^* and H_2O^* on the surface of electrocatalysts.51-53

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$$q^* = \frac{1}{vmS} \int_{E1}^{E2} i(E) dE \qquad \longrightarrow \qquad (1)$$

where q* is the estimated charge (mC cm⁻² mg⁻¹) which is directly proportional to the active sites of catalytic layer, v is the scan rate (V s⁻¹), m is the mass of catalyst (mg) loaded on the substrate, S is the geometrical surface area (cm²) of catalyst loaded substrate (CP), E1 and E2 is the range of scanning voltage in CV. The q* values under the redox peak (Ni²⁺/Ni³⁺) in the different electrocatalysts have been calculated and the results were shown in Fig S5. It clearly suggests that NiS₂ SCF-CP has more accessible active sites for the formation of surface hydroxides compared to NiO-CP and NiS₂ Sol-CP. Fig. 5b shows the LSV of OER of bare CP, NiS₂ SCF-CP, NiS₂ Sol-CP, NiO-CP, and IrO₂-CP at a scan rate of 2 mV s⁻¹ in 1 M KOH. It can be clearly seen that bare CP showed poor catalytic activity for OER compared to electrocatalysts modified CP. Among the modified CP, NiS₂ SCF-CP shows comparably close catalytic activity to IrO₂ and higher than NiO-CP and NiS₂ Sol-CP. In the metric relevant to derive the current density of 10 me Δ cm² (current density is approximately equal to 10% efficiency of solar to fuel conversion by one time sun light illumination), ⁵⁴ NiS₂ SCF-CP was delivered at 1.494 V vs. RHE, which results in an overpotential of 264 mV close to IrO₂-CP (260 mV). Whereas, NiO-CP and NiS₂ Sol-CP samples exhibited overpotential of 385 and 336 mV, respectively. It could be attributed to the presence of less accessible active sites for the adsorption of OH⁻ ions that is well supported by the Faradaic active site measurement. Further, the obtained catalytic activity for all the electrocatalysts were compared at an identical conditions (Fig. 5c).



Fig. 5 (a) CVs of different electrocatalysts modified CP, (b) LSV of bare CP and electrocatalysts (NiO, NiS₂ Sol, NiS₂ SCF and IrO₂) on CP at a scan rate of 2 mV s⁻¹ in 1 M KOH, (c) Comparison of catalytic activity of all the electrocatalysts under identical conditions and (d) Tafel plots of NiO, NiS₂ Sol, NiS₂ SCF and IrO₂ on CP.

It is persistent to note that current density (mA cm⁻²) of both electrodes (NiS₂ SCF-CP and IrO₂-CP) at constant η and the η at 10 mA cm⁻² is a close resemblance to each other. The comparable OER catalytic activity of NiS₂ SCF nanostructures to benchmark IrO₂ electrocatalyst are attributed to the sheet-like surface characteristics (Fig 3a-d&S3). Tafel slope ($\eta = a + b \log \frac{1}{2}$ (*j*); where η , a, b and *j* is the overpotential, constant, Tafel slope and current density, respectively) analysis was conducted to evaluate the kinetic behaviour of the different electrocatalysts are shown in Fig. 5d. It was noted that comparable Tafel slope value observed for NiS₂ SCF (105 mV dec⁻¹) and IrO₂ (95 mV dec⁻ 1) modified CP electrode. While, NiS₂ Sol-CP and NiO-CP showed the Tafel slope values of 112 and 126 mV dec⁻¹, respectively. The closest Tafel slope values of NiS₂ SCF and IrO₂ is again proves the close resemblance of their OER catalytic activities. It is worthy to mention here that the observed high Tafel slope values could be attributed to the diffusion limitation through the CP or Ni foam electrode.^{9,28,55-57} Though, the Tafel slope value of NiS₂ is much lower than that of recently reported literatures where the OER electrocatalysts are Ni_3S_2 in Ni foam

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(150-170 mV dec⁻¹) and Ni₃S₂/AT Ni foam (159.3 mV dec⁻¹).^{56,57} The obtained NiS₂ catalytic activity was compared with recent reports on different nickel sulphide system (Table S1).

The stability of NiS₂ catalyst was assessed through CV with accelerated scan rate (30 mV s⁻¹) for 500 cycles in the potential window of 1 to 1.7 V vs. RHE in 1 M KOH solution (Fig. 6a). It revealed that the catalytic activity is increase (n was decreased by ~26 mV) upon the electrochemical aging. In addition, the stability of NiS₂ catalyst was measured under the OER condition using chronoamperometry method at the applied potential of 1.7 V vs. RHE (Fig. 6b). It indicates that OER catalytic current density was increased with an increase in time. It is well consistent with the accelerated CV stability test and the previous reports on Ni containing OER catalysts.58-61 Based on the observations and previous reported literatures, the enhancement of NiS2 electrocatalytic activity upon the electrochemical aging is due to the formation of catalytically active nickel hydroxide/nickel (oxy) hydroxide intermediates by the reaction between NiO covered NiS₂ and KOH electrolyte. In addition, the significant decrease in sulphur from the NiS₂ surface was observed due to the dissolution of sulphur by continuous electrochemical cycling that was confirmed by XRF analysis (Fig. S6 & S7). Similar sulphur dissolution and the formation of oxygen rich surface were also observed in the previous studies on NiS@SLS, NiSx and NiSe2, 15,16,58,62 which are more responsible for an enhanced OER catalytic activity upon the electrochemical aging.^{16,58} Generally, the leaching of sulphur from the metal sulphide surface can be observed when the applied potential was > 1 V vs. RHE in alkaline condition.^{16,63}



Fig. 6 (a) Cyclic stability of NiS₂ SCF-CP at a scan rate of 30 mV s⁻¹ and (b) Chronoamperometric stability of NiS₂ SCF-CP at the applied potential of 1.7 V vs. RHE in 1 M KOH.

Charge transfer kinetics of different electrocatalysts during the OER was evaluated using EIS Nyquist plot (Z_{Real} vs Z_{Img}). Solution induced resistance (R_s) with the electrode/catalyst and charge transfer resistance (R_{ct}) by the redox reaction could be connected to OER kinetics; which was evaluated from the impedance spectrum fitting with Randles plot using the simple and most common equivalent circuit as inserted in Fig 7. Capacitance (C_{dl}) parallel with R_{ct} is due to the double-layer charging at electrode and solution interface. The measured R_s values are found to be 3.12, 2.82, 3.84 and 2.97 ohm for NiS₂ SCF-CP, NiS₂ Sol-CP, NiO-CP and IrO₂-CP, respectively. While, R_{ct} values are found to be 7.71, 20.28, 50.20 and 6.79 ohm for NiS₂ SCF-CP, NiS₂ Sol-CP, NiO-CP and IrO₂-CP, respectively. The observed closest R_{ct} value between NiS₂-SCF-CP (7,71 ohm) and IrO₂-CP (6.79 ohm) further confirms the existence of profile the catalytic activity in SCF assisted synthesized NiS₂ nanostructures that could replace the IrO₂ based electrocatalysts. Further, the observed EIS results well coinciding with previous LSV and Tafel slope analysis.

The possible mechanism for enhanced OER electrocatalytic activity and stability of NiS₂ catalyst can be described to the sheet-like nature of NiS₂. It provides the freely accessible active sites for catalytic OER initially and then the catalytically active metal hydroxide and metal (oxy)hydroxide (NiOOH); (M²⁺ \rightarrow M³⁺) intermediates were formed upon the continuous OER. In the meantime, a decrease of sulphur content is also enhancing the formation of active intermediates in the high alkaline condition.^{16,58} The similar increase in activity on Ni-based sulphur systems have also been observed extensively in the previous reported literatures.^{16,58,61,62,64}



Fig. 7 Nyquist plot of electrocatalysts measured at the η of 300 mV.

Conclusions

Noble metal free NiS₂ nanostructures were successfully synthesised by simple and one-pot SCF processing in a short reaction time of 60 min. Structural and morphological characterizations confirmed the formation of cubic NiS₂ nanostructures. Remarkably, the as-synthesized NiS_2 nanostructures showed the superior OER electrocatalytic activity with a low overpotential of 264 mV vs. RHE and a Tafel slope of 105 mV dec⁻¹. The obtained catalytic activity of NiS₂ nanostructures are very similar to that of benchmark IrO2 catalyst. Hence, the NiS₂ nanostructures are the promising material for the replacement of noble metal based (IrO₂) OER catalyst. In addition, SCF method is a facile and environmental benign method for the preparation of high quality crystalline nanomaterials in a short reaction time. Thus, the SCF method can be utilized for the synthesis of other metal sulphides/oxides for diverse applications.

Conflicts of interest

There are no conflicts of interest to declare.

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Graphical Abstract:

Supercritical Fluid Processing for the Synthesis of NiS₂ Nanostructures as Efficient Electrocatalyst for Electrochemical Oxygen Evolution Reaction

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A facile supercritical fluid process was demostrated for the synthesis of cubic NiS_2 nanostructures for efficient electrochemical oxygen evoltion reaction.