Schematic synthesis of cobalt-oxide (Co$_3$O$_4$) supported cobalt-sulfide (CoS) composite for oxygen evolution reaction

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Development of electrocatalysts has received great attention for storage and energy conversion technologies. Different electrocatalysts for oxygen evolution reaction (OER) have been produced and investigated but their role is not sufficient to mark of Ruthenium oxide (RuO$_2$). Therefore, it is global requirement to produce an efficient, lower cost and earth-abundant electrocatalyst for OER. Herein, cobalt oxide-cobalt sulfide (Co$_3$O$_4$-CoS$_2$) composite have been synthesized via hydrothermal chemical method with active performance OER. The desired overpotential is 280 mV to achieve current density of 20 mA cm$^{-2}$ of as prepared composite with Tafel slope value of 74 mV dec$^{-1}$. As prepared Co$_3$O$_4$-CoS$_2$ composite has efficient stability of 30 hours for long term electrochemical performance.

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1. Introduction

With increasing problems for global energy and environmental contaminations, utilization of electrocatalysts favor to get renewable energy source [1, 2]. The water splitting method has been considered as an important base of modern chemical process, it has significance for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) [3, 4]. HER and OER have a dynamic role for production of hydrogen energy with less environment contamination [5, 6]. An efficient, low cost and electrochemically stable electrocatalyst for OER is still challenge for water splitting. Previously, researchers have focused on substructure of efficient and earth abundant

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electrocatalysts [7, 8]. In previous studies, various precious metals have been reported such as Ir, and Ru base catalysts were utilized for OER applications as well. Due to their high cost, rare source and processing time make it still limited [9, 10]. OER is an essential reaction of electrochemistry that belong to storage system and power conversion, like fuel cells, water electrolyzes and metallic-air batteries [11, 12].

Some of the electrochemical characteristics of oxides have been used as cathodes and anodes in batteries or as electrocatalysts which have been reviewed briefly [13, 14]. In this regard, Jung et al. synthesized Co$_3$O$_4$ catalysts through transition of phase h-CoO into trigonal Co(OH)$_3$ with better stability and outstanding electrochemical response compared with pristine Co$_3$O$_4$ [15]. Yu et al. prepared disordered cobalt oxide nanostructure induced by sulfur (S-CoO$_x$) that lead to more defect sites and enhanced low oxygen coordination, these features exhibit higher activity and efficient sustainability in alkaline electrolyte. Gao et al. reported improved catalytic activity by surface nitridation of Nickel-cobalt alloy (Ni$_2$-CoN), and found fast surface reconstruction that accelerates good active sites and stable for oxygen evolution [16]. Electrode potentials and stoichiometric reactions for the potential determination of various metal oxides have been discussed [17, 18].

Transition metal based electrocatalysts have been reported as an effective alternative of noble metal based electrocatalysts for OER such as; sNiMs@NF [19], NiCo$_2$O$_4$ [20], Mn-Fe oxide. Metal oxides are considered as encouraging electrode materials for conversion systems and energy storage including lithium-ion batteries (LIBs), hybrid super capacitors (HSCs), metal air batteries (MABs), sodium ion batteries (SIBs) and so on. Previous research report; sulfides of cobalt, like Co$_2$S$_4$, CoS$_2$, CoS have an essential activity of catalyst toward OER and HER both in alkaline medium with better chemical strength and electrical conductivity. There are various methods have been reported to prepare transitional metal nano composites such as; Liquid metal infiltration, Vapor techniques (PVD, CVD) and electrodeposition.

In this study, hydrothermal chemical method has been executed to synthesize Co$_3$O$_4$-CoS$_2$ composite for active OER performance. Pristine Co$_3$O$_4$, pristine CoS and two composites were obtained by varying Co$_3$O$_4$ into CoS marked as Sample-1 and sample-2. An overpotential of 280 mV has been recorded to achieve 20 mA cm$^{-2}$ current density value with lower Tafel slope value of 74 mV dec$^{-1}$ by using Tafel equation. For morphology, crystallinity and chemical compound analysis SEM, XRD, TEM and FTIR were executed on pristine Co$_3$O$_4$, CoS and as prepared composites (sample-1 and sample-2). EIS and CV were performed to obtain charge transfer resistance (R$_ct$), double layer capacitance (C$_dl$) and electrochemical active surface area (ECSA) measurement respectively. Above mentioned merits and various electrochemical results have proved that Co$_3$O$_4$-CoS$_2$ composite is an encouraging electrocatalyst for promising water splitting and energy conversion framework.

2. Experimental work

All the chemicals have been used in this experiment are of analytical grade and applied directly without any further purification. Thiourea (CH$_3$N$_2$S), cobalt chloride hexahydrate (CoCl$_2$.6H$_2$O), potassium hydroxide (KOH), alumina slurry, and deionized water were purchased from Sigma-Aldrich Karachi.

Co$_3$O$_4$-CoS$_2$ composites were prepared by three phases. Initially, Co$_3$O$_4$ nano-structure was prepared by aqueous chemical growth process by taking 0.1M Cobalt chloride hexahydrate and 0.1M urea and placed for 5 h at 95$^\circ$C into electric oven instrument by FOTILE 52L. The precipitates were collected and washed by deionized water for several times. Later on, calcination process was adopted on as received powder form of cobalt at 500$^\circ$C in air to get its final product from hydroxide form. Finally, varying amount of 50 mg and 150 mg of Co$_3$O$_4$ were utilized for the decoration on CoS$_2$ by hydrothermal strategy at 200$^\circ$C for 24 h. Thiourea 100 mM and cobalt chloride 40 mM concentration were used for CoS$_2$ solution and finally Co$_3$O$_4$-CoS$_2$ composites were obtained through filtration. Same strategy was applied for production of pristine CoS.
The morphological attributes were studied by executing low resolution scanning electron microscopy (Phillips, model CM 200 at 20 kV) at an advancing 15 kV voltage range. X-ray diffraction (Philips powder X-shaft diffractometer) was utilized to analyze crystallinity of pure Co$_3$O$_4$, pure CoS and as prepared Co$_3$O$_4$:CoS$_2$ composite. Transmission electron microscopy instrument by FEI TECHNO G2 USA was used to determine the morphology of various nano materials in detail. FTIR instrument by PERKIN ELMER SPECTROPHOTOMETER was used for functional group study of various nanomaterials within wavenumber range of 400–4000 cm$^{-1}$.

The potentiostat machine by VERSA STAT4 was applied for different electrochemical tests. In three electrode mechanism Glassy carbon electrode (GCE) 3 mm diameter was used as working electrode, graphite bar as counter electrode and silver-silver chloride was used as reference electrode. At that point, 10 mg of every catalyst with 4 mL of deionized water was sonicated on ultrasonic bath to get proper homogeneous solution and 1 mL of 5% Nafion solution (as fastener) was used. 10 µ-liter of every Catalyst was covered on GCE and dried at room temperature, amount of impetus on GCE was about 0.30 mg cm$^{-2}$. Various electrochemical tests for OER activity were executed in 1M KOH solution. Initially linear sweep voltammetry was done by applying voltage ranges from 0 to 0.8V vs RHE. Cyclic voltammetry (CV) was carried with 0.1 to 0.25V at scan ranges from 30, 50, 70 and 90 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) was done at voltage range of 5mV at frequency ranges from 100 kHz to 0.1 Hz. Stability practice was done at 20 and 40 mA cm$^{-2}$ current densities through chronopotentiometry technique. Capacitance double layer ($C_{dl}$) values were calculated from CV curves of various nano materials. The results of EIS were illustrated by z-view software. Investigated potentials are described all over in manuscript in opposition to the reversible hydrogen electrode (RHE) through Nernst equation.

3. Results and discussion

Morphological study of different composites was analyzed via SEM as given in Fig. 1. Pristine CoS revealed round structure attributes containing various microns' level in Fig. 1(a). It reveals aggregation which is gathered by small flowery flakes. At contrasting, pure Co$_3$O$_4$ has been analyzed with nanoparticles as given in Fig. 1(b). While, Fig. 1(c) represents combined nanowire with round shape structures in sample-1 which shows availability of twice materials Co$_3$O$_4$ and CoS$_2$ in sample-1 (Co$_3$O$_4$:CoS$_2$ composite). Fig. 1(d) reveals structure of sample-2 containing mixture of round shape and nanowire with higher intensity due to addition of Co$_3$O$_4$ with more quantity. Co$_3$O$_4$:CoS$_2$ composite showed non-uniform morphologies as existence of two different attributes. Therefore, CoS$_2$ has a referable OER performance in sample-2 with various physical changes. At that point, the successful chemical growth of Co$_3$O$_4$ on CoS$_2$ can be observed through various SEM images.
XRD technique has revealed the crystalline arrays of pristine CoS, Co₃O₄ and prepared composite as shown in Fig. 2. The pristine CoS diffraction patterns are intensive and resolved well, as it is confirmed by JCPDS card number: (01-075-0605) with hexagonal shape. XRD confirms that Pristine CoS has no other state of contaminations. The pristine Co₃O₄ shows well acute patterns which meet with the JCPDS card number: (01-080-1534) with cubic crystalline phase. Furthermore, it reveals that Co₃O₄ is pure, except of any other region of cobalt containing hydroxide and oxide phases as per given reference. XRD analysis was carried out for sample-2 and cubic phase is found within CoS₂ by JCPDS card number: (00-003-0772) We have obtained both CoS₂ and Co₃O₄ in our as prepared Co₃O₄-CoS₂ composite material. XRD has assured that power of diffraction patterns of CoS₂ were decreased. Moreover, XRD study further described that Co₃O₄-CoS₂ has no any other phase of impurities.

Fig. 2. Diffraction patterns of Pure Cos, Co₃O₄ and Sample-2.
Transmission electron microscopy (TEM) has been executed on various nanomaterials to analyze their surface morphology in deep way as depicted Fig. 3.

![TEM images](image)

Fig. 3. TEM images of (a) Pristine Co$_3$O$_4$, (b) Pristine CoS, (c) Sample-1 and (d) Sample-2.

Pristine Co$_3$O$_4$ has revealed its morphology as agglomerated nanoparticles with agreement to previous study as depicted in Fig. 3(a). The TEM image of CoS has shown hierarchical hollow nano-cages in detail as shown in Fig. 3(b). Uniform CoS layers are consisting of monodispersed layered structure. These outer nanoparticles of CoS have rough surfaces type morphology. As prepared composites sample-1 and sample-2 have similar structural characteristics with changes in intensity of Co$_3$O$_4$ within CoS$_2$ as given in Fig. 3(c) and (d) respectively. There is existence of Co$_3$O$_4$ nanoparticles with varying quantity which is clearly observed at different boundaries in core of CoS$_2$ and outer bright translucent shell within sample-1 and sample-2. The successful synthesis of Co$_3$O$_4$-CoS$_2$ composite has been observed from various TEM images for synergetic electrochemical performance for OER activity.

The FTIR analysis was applied for pristine CoS, Co$_3$O$_4$ and as prepared composite electrocatalyst. IR spectra of Co$_3$O$_4$ nanocomposite is shown in supplementary information as Fig. (S1). Broad band at 3440 cm$^{-1}$ is because of stretching vibration mode of O–H group. Band around 848 cm$^{-1}$ is due to peaks of CO$_3^{2-}$ anions. Two peaks at 574 and 670 cm$^{-1}$ have correspondence to Co-O stretching vibration mode. Whereas, the relevant band at 1110 cm$^{-1}$ along with spectrum of CoS relevant to the N–H bending vibration. To evaluate structure of sample-2 via FTIR is also mentioned in given corresponding figure, another peak at 570 cm$^{-1}$ stretching vibrations of Co atoms have been observed on the surface of cobalt sulfide as relevant small peak.
Electrochemical tests of different electrocatalysts were studied in 1M KOH using three-electrode system for OER activity. LSV polarization strategy for CoS, Co$_3$O$_4$ and its composites Sample-1 and Sample-2 are shown in Fig. 4. It is highlighted that pure CoS and Co$_3$O$_4$ have not good OER activity, by addition of Co$_3$O$_4$ for good appearance of CoS$_2$ has dramatically increase in OER kinetics. Supplementary addition of Co$_3$O$_4$ for deposition has also shown great role in conductivity and capacitance as well. Sample-2 has more activity because of fast charge transport given through Co$_3$O$_4$ single dimensional nanowires, along with active sites from CoS$_2$ and good stoichiometry of Co presence has revealed essential OER kinetics. As prepared composite of Co$_3$O$_4$-CoS$_2$ marked as sample-2 has over all good OER response more than both of given pristine forms which is shown in Fig. 4(a).

The overpotential value of 280 mV is required to reach at current density of 20 mA cm$^{-2}$ for sample-2, which is better than sample-1 that has overpotential value of 355 mV. From LSV curves, Co$_3$O$_4$-CoS$_2$ composite material along with specific amount of Co$_3$O$_4$ can enhance OER performance of CoS$_2$. Meanwhile it could be an excellent alternative of noble metal containing electrocatalyst for OER. Tafel plot is essential factor for OER activity of electrocatalyst as rate-determination step, as shown in Fig. 4(b). It assured that pure CoS$_2$ and Co$_3$O$_4$ have poor electrochemical response. Sample-2 has Tafel slope value of 74 mV dec$^{-1}$ which is lowest toward cobalt based electrocatalyst for OER and nearer to Tafel slope value of RuO as 55 mV dec$^{-1}$. 

Fig. 4. (a) LSV curves of pure CoS, pure Co$_3$O$_4$, sample-1 and sample-2, (b) Tafel plots, (c) Durability practice, (d) Chronopotentiometry at 20 and 40 mA cm$^{-2}$ for 30 h, (e) Histogram for overpotential values.
Sample-1 has higher Tafel slope of 102 mV dec\(^{-1}\). Therefore, on the basis of Tafel slope analysis we can report that OER activity of Sample-2 is closer to noble metal based electrocatalyst. As depicted in Fig. 4(c) durability of sample-2 was analyzed before and after stability test. The chronopotentiometry technique was applied at 20 and 40 mA cm\(^{-2}\) current densities for stability, without any loss of potential was observed as clearly shown in Fig. 4(d). While corresponding overpotential value of every electrocatalyst is described in histogram as given in Fig. 4(e).

Basically, OER mechanism contains four electron transfer system which could be described over the surface of desired metal oxide in alkaline environment as given four steps below:

\[
\begin{align*}
M + OH^- & \rightarrow MOH + e^- \\
MOH + OH^- & \rightarrow MO^- + H_2O \\
MO^- & \rightarrow MO + e^- \\
2MO & \rightarrow 2M + O_2 + 2e^- 
\end{align*}
\]

Above given four steps mechanism has its theoretical Tafel values as per steps 1 to 4 are 120, 60, 40 and 15 mV dec\(^{-2}\). However, in this work the rate determining step for Co\(_3\)O\(_4\)-CoS\(_2\) electrocatalyst is step 3 as per obtained Tafel slope value from given relation.

\[
\eta = a + b \log(j)
\]

where \(\eta\) defines overpotential value, \(j\) defines current density and \(b\) defines Tafel slope respectively\(^{39}\).

To make more strength of polarization and Tafel curves, OER kinetics of electrocatalyst was measured through electrochemical impedance spectroscopy (EIS) in 1M KOH solution. The value of charge transfer rate has been defined via diameter of semicircle arc and analyzed \(R_c\) value for sample-1 is 280 \(\Omega\), that is higher than the composite of sample-2 which has value of 85 \(\Omega\) respectively. These both values are several times less than pristine CoS and Co\(_3\)O\(_4\) as obtained 1250 and 905 \(\Omega\). It has been confirmed that faster charge transport is related to Sample-2 composite is due to addition of Co\(_3\)O\(_4\). For similar electrochemical impedance spectroscopy results, bode plots were obtained as appeared in Fig. 5 (a) and (b) which support more to Nyquist plots. Nyquist plots of various composites are given in Fig. 5 (c). However, Cyclic voltammetry (CV) was applied at various scan rates for calculation of ECSA and \(C_{dl}\) as given in supplementary information which is depicted in supplementary file as Fig. (S2). CV was carried out at scan rate of 30, 50, 70 and 90 mV sec\(^{-1}\) for pristine CoS, Co\(_3\)O\(_4\) and composites sample-1 and sample-2 along with pristine GCE as its supportive information. The corresponding \(C_{dl}\) values are calculated as 4.0 \(\mu F\) cm\(^{-2}\) for pristine Co\(_3\)O\(_4\), 5.3 \(\mu F\) cm\(^{-2}\) for pristine CoS, 8.2 \(\mu F\) cm\(^{-2}\) for Sample-1 and highest one for sample-2 is 20 \(\mu F\) cm\(^{-2}\). The obtained ECSA values of various composites were calculated from \(C_{dl}\) values through given expression.

\[
ECSA = C_{dl} / C_s
\]

where, \(C_{dl}\) represent double layer capacitance value and \(C_s\) specific capacitance (i.e., \(C_s=0.04 \mu F\) cm\(^{-2}\)) for KOH environment. Through this expression, analyzed values of ECSA for various electrocatalysts are as 100, 132.5, 205 and 500 cm\(^{-2}\) for pristine Co\(_3\)O\(_4\), CoS, sample-1 and sample-2 which are mentioned below in Table 1. The enhanced value of ECSA for sample-2 put impact for addition of Co\(_3\)O\(_4\) as its vital role toward effective OER activity.
Fig. 5. EIS of pure CoS, pure Co$_3$O$_4$, Sample-1, Sample-2 by amplitude of 5 mV with frequency ranges from 100 KHz to 0.1 Hz, with settled potential of OER (a, b) bode plots (c) Nyquist plots (d) Corresponding $C_d$ values by linear fitting at different scan rates from CV curves for of Co$_3$O$_4$, CoS, sample-1 and sample-2.

Table 1. Unique Features of reported OER electrocatalysts.

| Catalyst       | Tafel Slope | Charge Transfer Resistance | Double Layer Capacitance | Electrochemical Active Surface Area |
|----------------|-------------|-----------------------------|---------------------------|-----------------------------------|
|                | $B$ (mV dec$^{-1}$) | $R_d$ (Ω)                  | $C_d$ ($\mu$F cm$^{-2}$) | ECSA (cm$^2$)                    |
| Co$_3$O$_4$ Pristine | 85          | 905                         | 4.0                       | 100                               |
| CoS Pristine    | 134         | 1250                        | 5.3                       | 132.5                             |
| Sample-1        | 102         | 280                         | 8.2                       | 205                               |
| Sample-2        | 74          | 85                          | 20                        | 500                               |

4. Conclusion

In conclusion, different substances are integrated containing pure CoS, Co$_3$O$_4$ and as prepared composites with varying ratio of Co$_3$O$_4$ via hydrothermal chemical strategies and analyzed for OER activity. This Co$_3$O$_4$-CoS$_2$ based electrocatalyst has indicated an incredible electrochemical performance for OER. Sample-2 displayed excellent electrical conductivity with lower overpotential value of 280 mV as compared to pristine Co$_3$O$_4$, pristine CoS and Sample-1 at 20 mA cm$^{-2}$ current density in alkaline environment. Moreover, durability of 30h was observed for Co$_3$O$_4$-CoS$_2$ (sample-2). The lower Tafel slope value of 74 mV dec$^{-1}$ with lower charge transfer resistance value 85 Ω for sample-2 proved it more active for oxygen evolution. As calculated larger ECSA value of 500 cm$^2$ has correspondence to more capacitive behavior of Co$_3$O$_4$-CoS$_2$ composite as well. SEM, XRD, TEM and FTIR have analyzed the morphology, crystallinity and
functional groups of various electrocatalysts. In this way, Co₃O₄-CoS₂ based electrocatalyst is well considered for a wide scope of energy conversion and electrochemical water splitting applications.

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Supplementary Material

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Fig. S1. FTIR spectra of pristine Co$_3$O$_4$, pristine CoS and prepared sample-2.
Table S1. Comparative study of recent reported electrocatalysts and current work.

| Electrocatlyst                      | Electrolyte | Current density | Overpotential | Tafel slope | Reference         |
|------------------------------------|-------------|----------------|---------------|-------------|-------------------|
| Sample-2 (Co₃O₄-CoS₂)             | 1M KOH      | 20 mA/cm²      | 280 mV        | 74 mV/dec   | This work         |
| Spinel Co₃O₄                      | 1M KOH      | 10 mA/cm²      | 296 mV        | 92 mV/dec   | [1]               |
| Ni-Co-F                            | 1M KOH      | 10 mA/cm²      | 326 mV        | 77 mV/dec   | [2]               |
| Mesoporous Co₃O₄ nanosheet         | 1M KOH      | 10 mA/cm²      | 290 mV        | 86 mV/dec   | [3]               |
| Ru/Ni-Co₃O₄                       | 1M KOH      | 10 mA/cm²      | 290 mV        | 70 mV/dec   | [4]               |
| Co₃S₂/Ni                          | 1M KOH      | 10 mA/cm²      | 283 mV        | 65 mV/dec   | [5]               |
| CoMn₃O₄-MSs                       | 0.1M KOH    | 10 mA/cm²      | 300 mV        | 72 mV/dec   | [6]               |
| CoS₂-TF                           | 1M KOH      | 10 mA/cm²      | 295 mV        | 57 mV/dec   | [7]               |
| MOF-driven CoS₂                    | 1M KOH      | 10 mA/cm²      | 298 mV        | 98 mV/dec   | [8]               |

Fig. S2. CV curves with varying scan rates of 30, 50, 70 and 90 mV/sec in 1M KOH (a) pure CoS, (b) pure Co₃O₄, (c) sample-1, (d) Sample-2.

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