



# Novel lanthanum sulfide–decorated zirconia nanohybrid for enhanced electrochemical oxygen evolution reaction

F. F. Alharbi<sup>1</sup> · Mehar Un Nisa<sup>2</sup> · Hassan Mohamed Ahmed Hassan<sup>3</sup> · Sumaira Manzoor<sup>2</sup> · Zahoor Ahmad<sup>4</sup> · Abdul Ghafoor Abid<sup>2</sup> · Salma Aman<sup>5</sup> · Muhammad Naeem Ashiq<sup>2</sup> · Karam S. El-Nasser<sup>6,7</sup> · Taha Abdel Mohaymen Taha<sup>8,9</sup>

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## Abstract

Metal sulfide and oxides have drawn interest as economical substitutes to noble metal catalysts due to their ability for oxygen evolution reaction (OER) activities. The inability of many sulfides and oxide nanocomposite materials has been produced in recent years to significantly boost their low OER activity. In the current study, we fabricated a novel lanthanum sulfide ( $\text{La}_2\text{S}_3$ ) nanocrystal decorated on zirconium dioxide ( $\text{ZrO}_2$ ) nanoflakes for OER electrocatalyst. The composite attains a low overpotential of 280 mV at a current density of 10 mA/cm<sup>2</sup> and outstanding stability of 30 h. The increased catalytic activity of the Zr–O–O superoxo group is responsible for the transfer of electron tendency from La species to  $\text{ZrO}_2$ , which favors the rupture of the bond of Zr–O in the steady arrangement. Hence, the present work developed an efficient  $\text{La}_2\text{S}_3$ -decorated  $\text{ZrO}_2$ -based oxygen evolution electrocatalyst instead of using rare earth viable catalysts like ruthenium oxide ( $\text{RuO}_2$ ) or iridium oxide ( $\text{IrO}_2$ ).

**Keywords** Water splitting · Nanohybrid ·  $\text{La}_2\text{S}_3/\text{ZrO}_2$  · OER · Alkaline media

✉ Muhammad Naeem Ashiq  
naeembzu@bzu.edu.pk

<sup>1</sup> Department of Physics, College of Science, Princess Nourah bint Abdulrahman University (PNU), P.O. Box 84428, Riyadh 11671, Saudi Arabia

<sup>2</sup> Institute of Chemical Sciences, Bahauddin Zakariya University, Multan 60800, Pakistan

<sup>3</sup> Department of Chemistry, College of Science, Jouf University, Sakaka 2014, Saudi Arabia

<sup>4</sup> Department of Chemistry, University of Engineering and Technology (UET), Lahore, Pakistan

<sup>5</sup> Department of Physics, Khwaja Fareed University of Engineering and Information Technology, Abu Dhabi Road, Rahim Yar Khan, Pakistan

<sup>6</sup> Chemistry Department, College of Science and Arts, Jouf University, P.O. Box 756, Al-Gurayat, Saudi Arabia

<sup>7</sup> Chemistry Department, Faculty of Science, Al-Azhar University, Assiut 71524, Egypt

<sup>8</sup> Physics Department, College of Science, Jouf University, P.O. Box 2014, Sakaka, Saudi Arabia

<sup>9</sup> Physics and Engineering Mathematics Department, Faculty of Electronic Engineering, Menoufia University, Menouf 32952, Egypt

## Introduction

Scientists have been working hard to invent efficient, low-cost, ecologically acceptable alternative energy conversion and storage methods to fulfill rising energy demands as well as those have no hazardous effect on the environment [1–6]. Electrolysis cells [7], fuel cells [8], and metal-air batteries [9] are only a few of the ways in which the chemical energy is turned into electrical energy. These devices go through steps with sluggish multi-electron transfer mechanism of both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) [10–13]. Engineering economical, high-efficiency electrocatalysts for OER are crucial for renewable energy systems [14]. Precious metal catalysts with high catalytic performance include Pd and few other precious metals, like Ag, Au, Ru, Ir, and Pt. Furthermore, Gokhan et al. synthesized the Ag/AgO-based nanocomposite employed toward water splitting process. The electrochemical result revealed that Ag/AgO nanoparticle exhibited 600 mV overpotential at 1 mA/cm<sup>2</sup> current density and lower Tafel slope of 80 mV/dec [15]. Yeo and Bell developed the cobalt oxide decorated on surface of Au nanoparticles employed toward electrocatalytic water splitting [16].

However, the electrocatalytic water splitting results of Ru, Ir, and Pt display the Tafel slope of 44, 64, and 143 mV and onset potential of 1.54, 1.56, and 1.86 potential at 0.5 mA/mol  $10^9$ /V, respectively, and suggest that noble metals are potential candidate for oxygen evolution reaction [17–19]. Due to their high cost and rarity, their commercial uses are limited [20]. On the other hand, the performance of an OER electrocatalyst is greatly influenced by pH of the electrolytes. An alkaline solution, rather than a neutral or acidic solution, is best for OER electrocatalysis. In recent studies, different transition metals show variable behavior in different electrolyte medium. However, noble metals such Pt, Ir and Ru shows great OER activity in alkaline as well as acidic medium [21]. Furthermore, She et al. studied the Ir-based electrocatalyst under the acidic medium for the oxygen evolution reaction process which exhibited an overpotential of 0.37 V [22]. Xu et al. synthesized IrRu@Te and employed toward OER activity in the acidic medium (0.5 M  $H_2SO_4$ ). The electrochemical result revealed that fabricated electrode display stability for 20 h and 50 mV overpotential at 10 mA/cm<sup>2</sup> current density [23]. However, Zhang et al. synthesized a Ru-based NiMo electrocatalyst and studied their electrochemical performance by employing toward OER activity result display the lower Tafel slope value of 110 mV/dec and 280 mV overpotential at the current density of 10 mA/cm<sup>2</sup> under 1 M KOH [24]. So in most of the cases, the OER efficiency was excellent in alkaline media therefore in the present work alkaline media has been chosen.

Various non-noble electrode materials have been studied in the OER process as prospective of noble metal electrodes replacements. Due to their electrocatalytic activity and non-noble metallic character, metal-free carbon compounds [25, 26], metallic alloys [27], metal oxides [28], metallic phosphides (MP) [29], metallic selenides (MS) [30], and carbon nitrides (CN) [31] have all been widely searched for OER [32]. The electrocatalysts due to their unique properties of an incompletely filled d-shell and increased electrical and thermal conductivity [33–35]. Non-precious metal-based compounds have been searched to avoid the usage of precious electrocatalysts in OER [36, 37] to reduce the sluggish OER kinetics [11]. A standard metric for determining this type of functionality (catalyst efficiency) is the potential difference ( $E$ ) measured against the reversible hydrogen electrode (RHE) [38].

The transition metal sulfides, including Co [39], Cu [32, 40], Ni [41], and La [42], showed better efficiency as an OER catalysts which have been discovered in the last decade [43]. When compared to other precious catalysts like, Ru/C (1.01 V) [44] and Ir/C (0.85 V) [45], many researchers such as Liu et al. reported that IrO<sub>2</sub>/ZrO<sub>2</sub> having Tafel

slope of 15 mV/dec [46]. Li et al. reported Ni(OH)<sub>2</sub>/ZrO<sub>2</sub> Tafel slope of 57 mV/dec in alkaline media [47]. To achieve a potential value of 263 mV, Mane et al. employed a one pot solvothermal approach to synthesize La<sub>2</sub>S<sub>3</sub>-MnS [42]. However, According to our findings, the catalytic activity of lanthanum sulfide substance in OER has been significantly improved than the previously estimated combined effect of OER. As a result, a high-performance lanthanum sulfide catalyst for OER has been developed.

Lanthanum sulfide must have active lanthanum sites to be used as an electrocatalyst. According to a prior study, the microchemical environment around the inner transition metal sites are preferable on metal-based catalysts [48]. Doping ions, supports, or other functional compositions can boost the activity of lanthanum centers [49, 50]. The synergetic effects of chemical coupling can lead to improved catalytic activity in composite catalysts as the OER performance of this catalyst is poor when performed as individual catalysts [51]. But single lanthanum sulphide has not good stability, and therefore, its composite with zirconia has been investigated. The titanium oxide has been widely used for various applications, and the zirconia is an isoelectronic with titania, and therefore, zirconia has been chosen as other material.

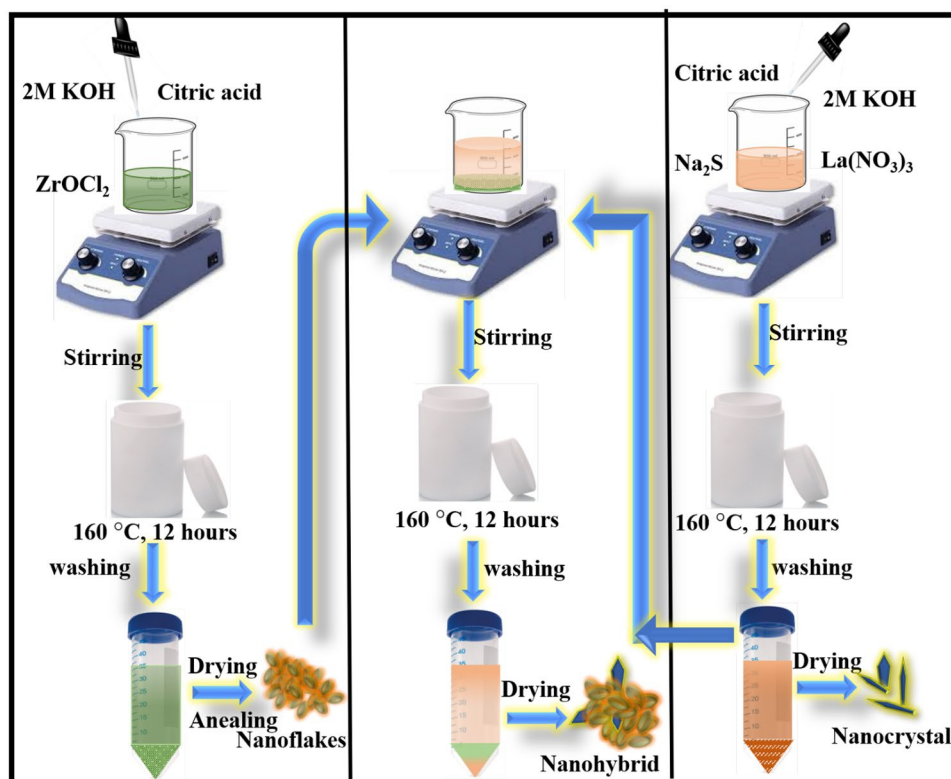
From the above motivated concern, herein, a highly active and stable OER electrocatalyst (La<sub>2</sub>S<sub>3</sub> nanocrystals decorated on ZrO<sub>2</sub> nanoflakes) has been developed via hydrothermal technique. Precious metal-based catalysts in an alkaline electrolyte performance have been comparable with materials synthesized in the present work regarding OER activity. The Zr-O bond is anticipated to be broken in the stable state due to electron transfer between La and ZrO<sub>2</sub> (Zr-O-O superoxo group), enhancing the electrocatalytic performance. Hence, due to its outstanding OER performance, La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> nanocomposite is a novel and potentially nonprecious oxygen evolution catalyst which can be used in future applications.

## Experimental technique

### Materials and methods

The zirconium dichloride oxide (ZrOCl<sub>2</sub>), sodium sulfide nanohydrate (Na<sub>2</sub>S·9H<sub>2</sub>O) VETEC (98%), lanthanum nitrate hexahydrate (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), potassium hydroxide (KOH), citric acid, (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), Duksan hydrochloric acid (HCl) Merck (37%), ethanol (C<sub>2</sub>H<sub>5</sub>OH), Analar (99%), acetone (CH<sub>3</sub>COCH<sub>3</sub>) Normapur (99.8%), nitric acid (HNO<sub>3</sub>), and ultrapure water.

**Scheme 1** Schematic illustration for the synthesis of all required products



### Synthesis of $\text{ZrO}_2$

A zirconium dioxide nanoflake was synthesized using a hydrothermal technique. The 0.05 M zirconyl chloride and 2.0 M KOH solutions were prepared in deionized (DI) water separately, and 0.1 mM solution of citric acid was also added to the zirconyl chloride solution. The solution of KOH was then added drop-by-drop in the solution mentioned above. The entire solution was transferred into a 100 mL Teflon-lined (T.L) autoclave and placed for 12 h at 160 °C in an oven. At room temperature, the autoclave was allowed to cool after 12 h. Subsequently, the obtained precipitates were centrifuged and washed many times with DI water and ethanol which were finally dried overnight at 80 °C. After that, the resultant precipitate was ground and annealed for 3 h at 450 °C in the furnace. The powder was collected and kept for further procedure.

### Synthesis of $\text{La}_2\text{S}_3/\text{ZrO}_2$

Nanohybrid  $\text{La}_2\text{S}_3/\text{ZrO}_2$  was synthesized using the hydrothermal technique. In this case, 0.05 M solution of lanthanum nitrate was prepared in deionized water, and 0.1 mM citric acid was also mixed under stirring. The weighed amount of already fabricated  $\text{ZrO}_2$  (equivalent to 0.05 M) was also mixed and stirred for a further 3 h to homogenize it. After that, sodium sulfide (0.05 M) was added to the above mixture and placed on the magnetic hotplate with continuous stirring.

After 3 h of constant stirring, solution was transferred to a T.L autoclave and kept in an electric oven at 160 °C for 12 h. The autoclave was cooled to room temperature, and the obtained precipitates were centrifuged and washed many times with DI water, ethanol, and dried overnight at 80 °C. A similar method was used to synthesize  $\text{La}_2\text{S}_3$  for comparison purposes except the addition of  $\text{ZrO}_2$  (Scheme 1).

### Physical characterizations and electrode preparation

X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), and x-ray photoelectron spectroscopy (XPS) analyses was used for the characterization of fabricated materials to confirm the structural, morphological, and surface properties. A Bruker D8 Advance Powder X-ray diffractometer was used to conduct XRD experiments on monochromatized  $\text{CuK}\alpha$  (0.15407 nm). The BET surface area, pore size, and pore volume were confirmed using NOVA-2200 E. On the other hand, the drop cast technique was utilized to make  $\text{La}_2\text{S}_3$ ,  $\text{ZrO}_2$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  thin films of constant thicknesses (0.001 mm) on stainless steel substrate and was used as a working electrode. Before being employed as substrates, the stainless-steel plates ( $1 \times 2 \text{ cm}^2$ ) were etched with oxalic acid, washed, and rinsed with deionized water. Electrochemical performances like linear sweep voltammetry (LSV), cyclic voltammetry

(CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry were performed to examine the electrocatalytic activity of La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> nanocomposite in 1.0 M KOH aqueous electrolyte.

## Electrochemical characterizations

AUTOLAB (PGSTAT-204) electrochemical workstation was used to manage the electrochemical investigation of fabricated materials using three-electrode setup. This experiment contains a catalyst-coated stainless-steel electrode, a Pt wire, and Ag/silver chloride as working, counter, and reference electrodes (saturated with 3.0 M KCl), respectively. Standard reversible hydrogen electrode (RHE) potential is calculated from the Ag/AgCl potential using the formula (1) for all viable measurements [52].

$$E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.059 \text{ pH} \quad (1)$$

The expression (2) was used to obtain the overpotential value:

$$\eta = E_{\text{vs RHE}} - 1.23 \text{ V} \quad (2)$$

The turnover frequency is another parameter to consider the material's catalytic effectiveness in an oxygen evolution reaction. It exhibits the ability of a catalyst to convert a substrate into a product in a unit of time under specific conditions. The following equation was used to calculate the turn over frequency of synthetic material.

$$\text{TOF} = I \times A / 4 \times F \times m \quad (3)$$

Here,  $I$  indicate the current at a specific overpotential,  $A$  is the geometrical surface area,  $F$  represents the Faraday's constant, and  $m$  is the number of moles of active catalyst.

In the presence of Ag/AgCl, the LSV was performed at a different scan rate in 1.0 M KOH with the voltage fluctuating between 0.02 and 0.07 V/s. As a result, the oxygen evolution currents start to change slightly. The electrochemical measurement were performed in 1.0 M alkaline electrolyte (KOH) with a potential range of 1.00 to  $-1.00$  V (against Ag/AgCl). A stability test was carried out using chronoamperometric recorded at 0.75 V applied potential. Electrochemical impedance spectroscopy (EIS) was done at open circuit potentials with frequencies ranging from 100 kHz to 10 MHz. The amplitude employed in EIS testing was set at 5 mV, taking the potential applied of 0.50 V.

## Results and discussion

### Structural analysis

The structure and phase orientation of all the fabricated samples were analyzed using powder X-ray diffraction (PXRD).

The powder X-ray diffraction pattern of synthesized La<sub>2</sub>S<sub>3</sub>, ZrO<sub>2</sub>, and La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> with their standard JCPDS pattern in the range of  $2\theta = 20\text{--}80^\circ$  is shown in Fig. 1. The diffraction peaks of La<sub>2</sub>S<sub>3</sub> demonstrated at  $2\theta = 20.8^\circ, 24.2^\circ, 28.5^\circ, 29.5^\circ, 31.2^\circ, 34.6^\circ, 35.1^\circ, 38.3^\circ, 39.9^\circ, 41.2^\circ, 43.5^\circ, 44.2^\circ, 49.4^\circ, 50.3^\circ, 54.1^\circ, 55.7^\circ, 57.3^\circ, 60.5^\circ, 62.7^\circ, 65.3^\circ, 71.2^\circ, 75.9^\circ,$  and  $77.0^\circ$  are well-matched with JCPDS No. 00–022–0645 indicating that there is no impurity phase. The diffraction peaks of the ZrO<sub>2</sub> were indexed at  $2\theta = 24.5^\circ, 27.3^\circ, 31.4^\circ, 34.3^\circ, 35.2^\circ, 38.2^\circ, 40.7^\circ, 45.3^\circ, 48.9^\circ, 50.3^\circ, 54.1^\circ, 55.4^\circ, 57.6^\circ, 59.1^\circ, 61.5^\circ, 62.3^\circ, 65.6^\circ, 69.1^\circ, 71.0^\circ, 72.8^\circ, 74.6^\circ,$  and  $78.1^\circ$  (JCPDS No. 00–001–0750) belonging to space group P2/c and space group number 13. The sharp peaks define the crystalline nature of the prepared La<sub>2</sub>S<sub>3</sub>, ZrO<sub>2</sub>, and La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub>. There is no undesirable diffraction peak appeared in the nanocomposite, endorsing the purity and successful synthesis of the composite. Hence, the nano-hybrid La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> contains all the peaks of its counterparts with a slight change in its peak position and intensity.

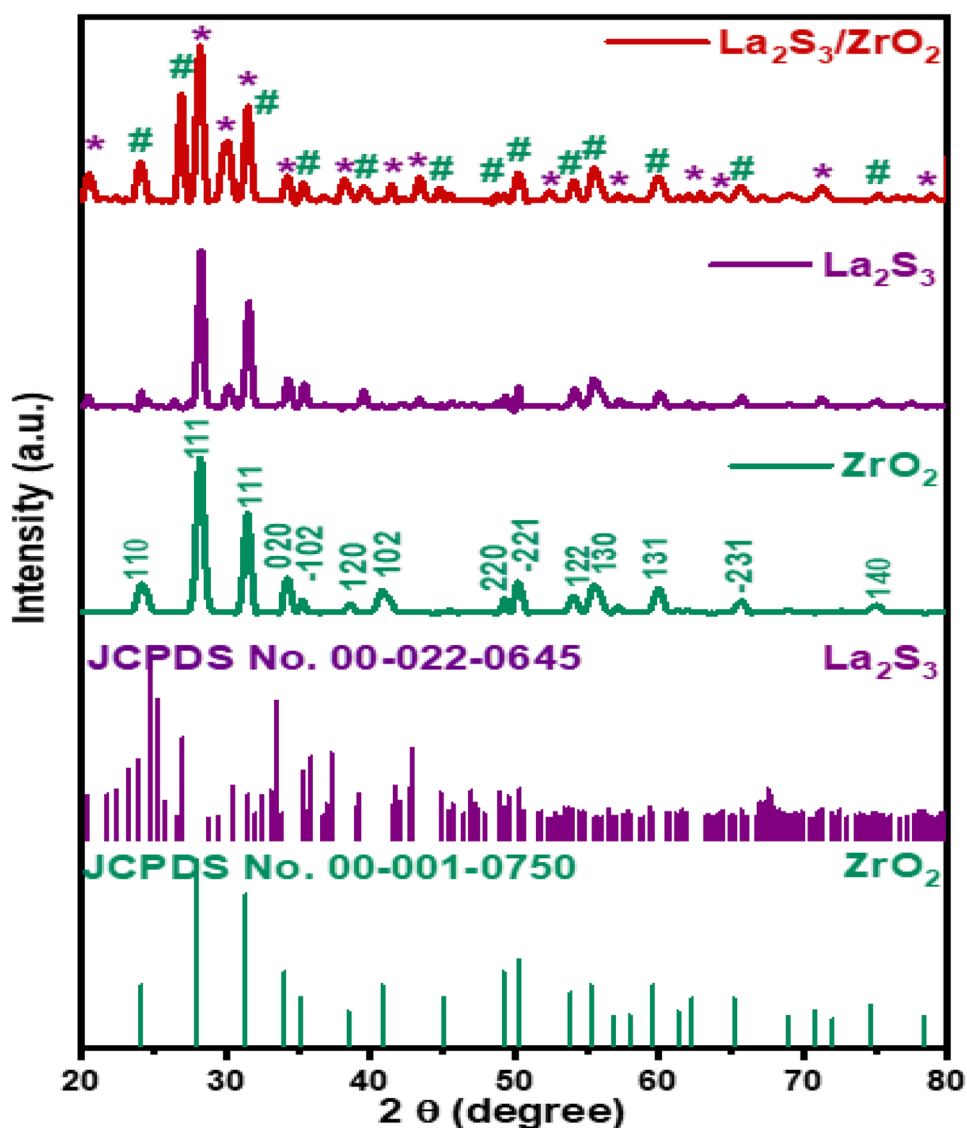
### Morphological analysis

The morphology and size of the material played a significant role in the variation of electrochemical parameters. Scanning electron microscopy studied the La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> nanohybrid and its counterparts, i.e., La<sub>2</sub>S<sub>3</sub>, ZrO<sub>2</sub> materials synthesized by hydrothermal route as shown in Fig. 2a–d. The obtained ZrO<sub>2</sub> and La<sub>2</sub>S<sub>3</sub> are infused nanoflakes and nanocrystals shape, respectively (Fig. 2a, b). The growth of the nanocrystals of La<sub>2</sub>S<sub>3</sub> on the ZrO<sub>2</sub> fused nanoflakes forming nanohybrid as displayed in Fig. 2c, d. The surface of the ZrO<sub>2</sub> is packed with La<sub>2</sub>S<sub>3</sub> particles ranging in size from 250 to 400 nm, and they appear to be distributed throughout the material. The ZrO<sub>2</sub> is filled with irregular La<sub>2</sub>S<sub>3</sub> nanocrystals, as shown in micrographs (Fig. 2c, d). Hence, the modified morphology of La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> plays a significant role in nanohybrid formation as well as in electrochemical properties. The EDX spectrum of La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> are shown in Fig. 2e. Only lanthanum, sulphur, zirconium, and oxygen elements were found, and no other element was found, proving the synthesized La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> material.

### XPS analysis

XPS spectra examined the synthesized material. Using Gaussian fitting, the deconvoluted peaks were obtained for deep study. According to the survey spectrum of La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> comprising only La, S, Zr, C, and O, as displayed in Fig. 3a, there is no other element except the investigated material which was also confirmed by the EDX analysis. Using the curve fitting approach, three Gaussian peaks were detected for the O 1s core level, as shown in Fig. 3b. Metal–oxygen is visible in the first peak at 530.2 eV, and

**Fig. 1** XRD pattern of  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$  with their respective standard reference patterns and  $\text{La}_2\text{S}_3/\text{ZrO}_2$



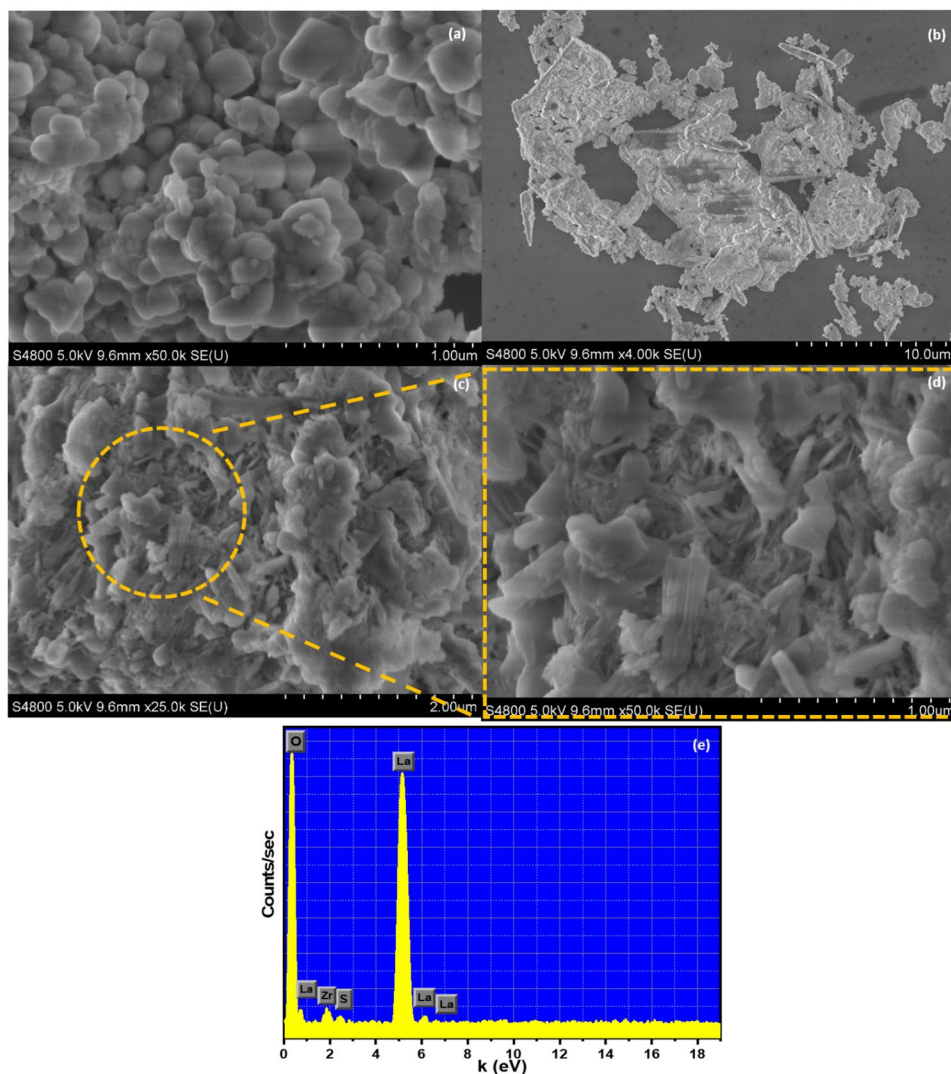
the last peak which was found at 532.5 eV corresponds to  $\text{O}_2$ . The 285 eV C 1 s peak seen in Fig. 3c is used for XPS peak correction. Peaks that can be found on the high beam-energy side of the La 3d are assigned to  $3d_{5/2}$ , and  $3d_{3/2}$  for the peaks at 834.2 and 851.2 eV, correspondingly resulting in +3 oxidation state (Fig. 3d). In the high-resolution S 2p spectrum, an exceedingly faint doublet at 163.3 eV corresponds to S 2p<sub>1/2</sub>, as shown in Fig. 3e, and the presence of oxygen sulfur (O-S) connection in the molecule is confirmed by the peak at 167.7 eV confirming the -2-valance state for sulphur. The fitted spectra of the Zr 3d spin-orbit doublet peaks are presented in Fig. 3f with a 2.1-eV energy separation having binding energy at 181.8 and 183.9 eV correlated to Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> contributions, correspondingly confirming the +4-valence state of Zr. This proved the successful formation of the  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite.

The Fig. 3g the material adsorption/desorption isotherm resultant from BET had mesoporous structures such as the H3 hysteresis loop. The consequent surface areas of  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite were 340 m<sup>2</sup>/g, 455 m<sup>2</sup>/g, and 612 m<sup>2</sup>/g, respectively. The resultant pore volumes for the  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  were 0.91, 1.12, and 2.05 cm<sup>3</sup>/g, respectively. Among all, the  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite may have better electrocatalytic activity than either  $\text{La}_2\text{S}_3$  and  $\text{ZrO}_2$  due to its larger surface area, pore volume, porosity, and more active sites on the surface.

### Electrochemical performance

The performance of  $\text{La}_2\text{S}_3$ ,  $\text{ZrO}_2$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nano-hybrid deposited on stainless steel strip (SSS) in 1.0 M KOH solution was investigated using LSV at a scan rate of 5 mV/s after electrochemical preconditioning with 20

**Fig. 2** SEM micrographs of **a**  $\text{ZrO}_2$ , **b**  $\text{La}_2\text{S}_3$ , **c**  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite, **d** enlarged SEM micrograph, and **e** EDX of  $\text{La}_2\text{S}_3/\text{ZrO}_2$

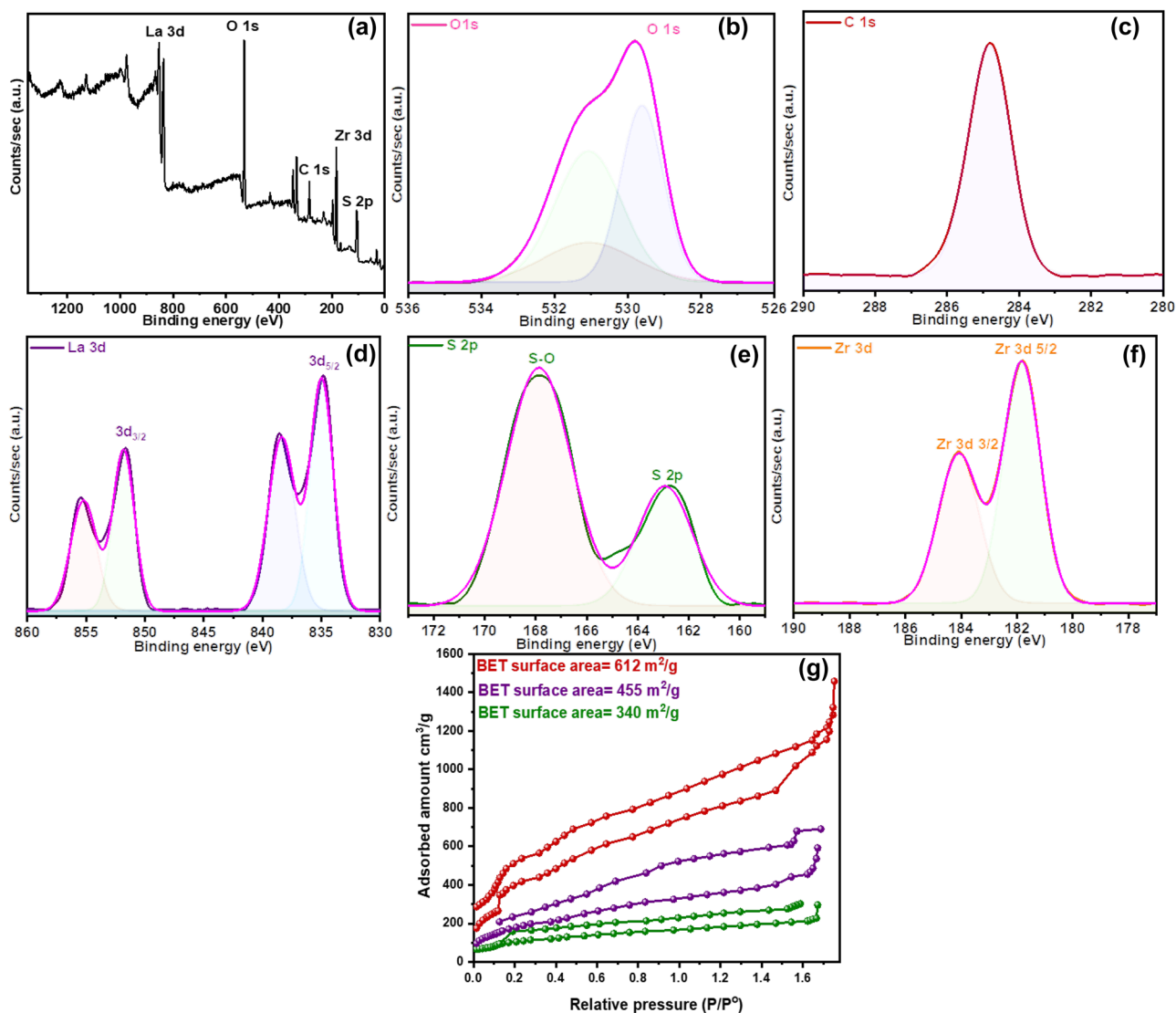


cyclic voltammetric scans using the three-electrode system. Figure 4a shows the linear sweep voltammogram of all the synthesized products and state of the art  $\text{RuO}_2$  material deposited on the stainless-steel surface. Among all the fabricated materials, the nanocomposite behaves a remarkable response to achieve oxygen evolution content. The enhanced efficiency of the nanohybrid was due to the presence of transition metal ions that can be employed as donor–acceptor chemisorption sites, and also, high conductivity can be achieved by hopping between cations with different valence states. The  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite showed the onset potential closest to the other rare metal and much lower than the  $\text{La}_2\text{S}_3$  and  $\text{ZrO}_2$ . In the nanocomposite, the synergistic effect occurs considering  $\text{ZrO}_2$  and  $\text{La}_2\text{S}_3$ , which is principally responsible for the significant OER activity.

The OER performance of the prepared samples was determined by another important parameter, such as overpotential

at a current density of  $10.0 \text{ mA/cm}^2$  using  $1.0 \text{ M}$  alkaline  $\text{KOH}$  solution. The resultant overpotentials of  $\text{La}_2\text{S}_3$ ,  $\text{ZrO}_2$ ,  $\text{RuO}_2$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite were 390, 420, 320, and 280 mV, respectively, as shown in Fig. 4b. On the other hand, the overpotentials of the composite material at current densities of 50 and  $100 \text{ mA/cm}^2$  were found to be 521 and 656 mV, respectively. The lower value of the overpotential for composite indicates better catalytic performance for OER because the single metal sulfides are less stable than transition metal oxide/hydroxide. Even though the  $\text{La}_2\text{S}_3/\text{ZrO}_2$  still outperforms many other catalysts when tested with a stainless-steel electrode at a current density of  $10.0 \text{ mA/cm}^2$  due to the presence of both sulfides and oxides, as given in Table 1. Hence, the resultant comparison analysis shows that  $\text{La}_2\text{S}_3/\text{ZrO}_2$  product has remarkable catalytic activity.

Figure 4c shows the results for calculating the catalyst's intrinsic electrocatalytic activity using their turnover



**Fig. 3** a Survey spectrum of the nanohybrid; XPS spectrum for b C1s, c O1s, d S 3d, e La 3d, f Zr 3d, and g BET isotherm of  $\text{La}_2\text{S}_3/\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ , and  $\text{ZrO}_2$

frequencies (TOFs). The TOF can be calculated via the Eq. (3) relation as [12]. The calculated TOF for  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  were 0.0006/s, 0.0019/s, and 0.0025/s, respectively. The results depict that  $\text{La}_2\text{S}_3/\text{ZrO}_2$  has the highest TOF at 1.5 V, which is 0.105 times higher than  $\text{ZrO}_2$  and 0.09 times that of  $\text{La}_2\text{S}_3$ . The greater the TOF, the higher will be the efficiency of the catalyst.

The Nyquist plots from the EIS measurements are examined under basic conditions using an equivalent circuit fitting, as shown in Fig. 4d. The charge transfer resistance (Rct) of  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  were 83.77  $\Omega$ , 81.49  $\Omega$ , and 40.12  $\Omega$ . When comparing the various Rct values, it is clear that the fabricated nanocomposite significantly improves charge transfer efficiency and, as a

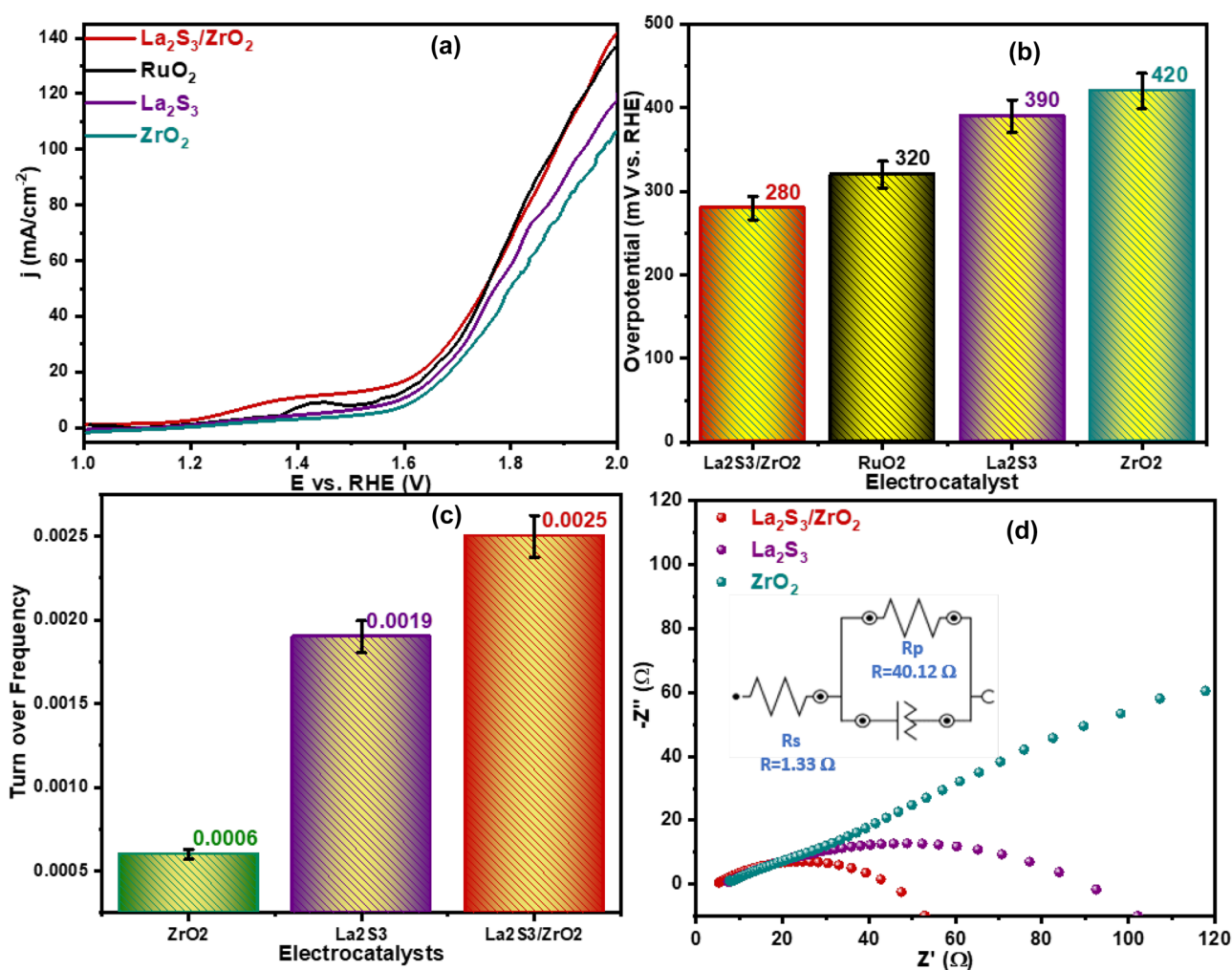
result, OER kinetics due to the synergistic effect between  $\text{ZrO}_2$  and  $\text{La}_2\text{S}_3$ .

Electrochemical surface area (ECSA) can be determined using cyclic voltammetry in non-Faradaic regions and was calculated using the following relation [62]:

$$C_{dl} = \text{slope}/2 \quad (4)$$

$$\text{ECSA} = C_{dl}/C_s \quad (5)$$

Slope of the plot  $\Delta j$  vs. scan rate is divided by 2 for the calculation of  $C_{dl}$  and by considering the specific capacitance value ( $C_s = 0.04 \mu\text{F}/\text{cm}^2$ ) as reported previously for all flat electrodes. The calculated ECSA for  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ ,



**Fig. 4** **a** Linear sweep voltammogram, **b** overpotential comparison, **c** Turn over frequency, and **d** EIS for  $\text{ZrO}_2$ ,  $\text{La}_2\text{S}_3$ , and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  (inset circuit diagram) in the alkaline environment for OER

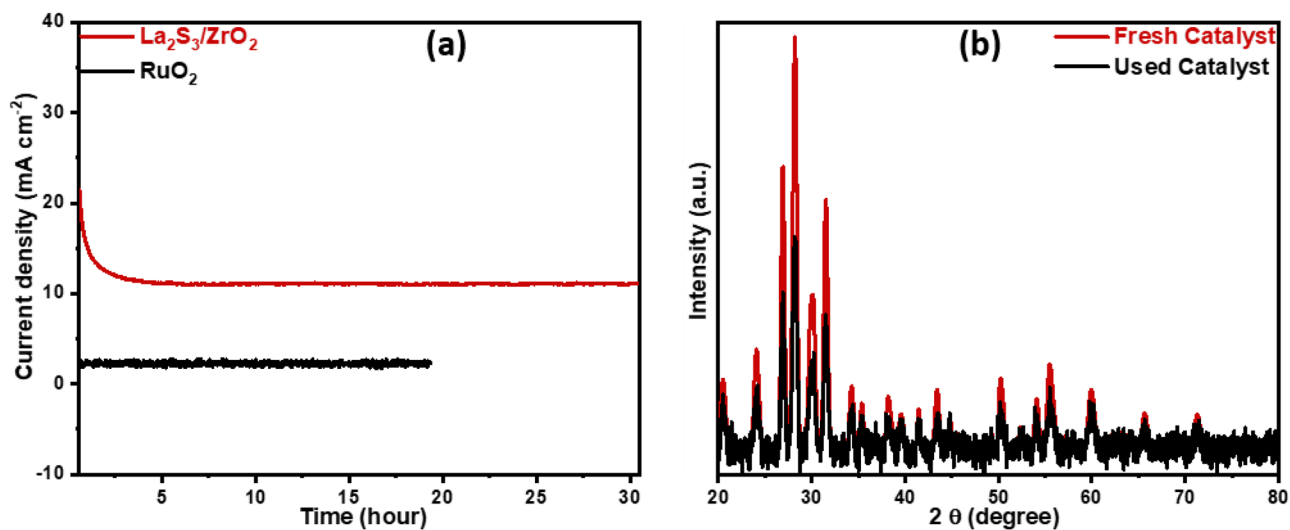
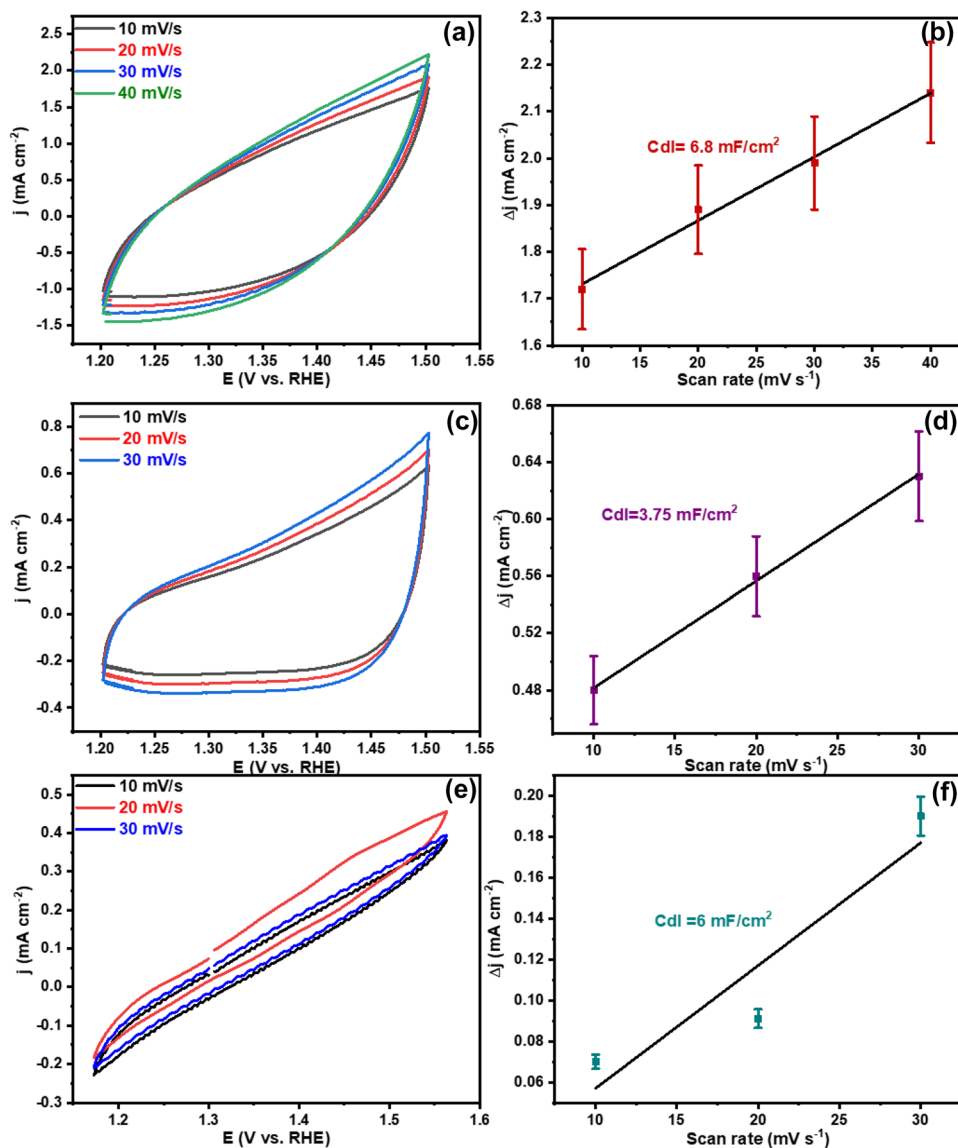
and  $\text{La}_2\text{S}_3/\text{ZrO}_2$  were  $93.75 \text{ cm}^2$ ,  $150 \text{ cm}^2$ , and  $170 \text{ cm}^2$ , respectively. It was shown in Fig. 5 that  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite has the highest  $C_{dl}$  ( $6.8 \text{ mF/cm}^2$ ) and ECSA ( $170 \text{ cm}^2$ ), which indicates that a higher ECSA allows for more electrochemical active sites and thus improves OER activity.

The long-term stability of catalytic electrodes is crucial in commercial applications. We investigated the OER stability of the  $\text{La}_2\text{S}_3/\text{ZrO}_2$  composite in an alkaline electrolyte using the (i-t) curve via chronoamperometry. Figure 6 shows the i-t

graph of the  $\text{La}_2\text{S}_3/\text{ZrO}_2$  composite and responds a straight line with just a slight drop, confirming the high stability of the composite material for electrochemical water oxidation up to 30 h, as shown in Fig. 6a. To confirm the stability of the resultant material after long term of 30 h stability, XRD analysis was performed, showing that the phase structure remains same while a little bit intensity of the peaks was changed as shown in Fig. 6b. Hence, the  $\text{La}_2\text{S}_3/\text{ZrO}_2$  nanocomposite performs the promising OER electrocatalyst because of its high OER activity and long-term stability.



**Fig. 5** a, c, e CV curves; b, d, f double-layer capacitance of  $\text{La}_2\text{S}_3/\text{ZrO}_2$ ,  $\text{ZrO}_2$ , and  $\text{La}_2\text{S}_3$



**Fig. 6** a Chronoamperometry; b XRD pattern before and after electrochemical study of  $\text{La}_2\text{S}_3/\text{ZrO}_2$

**Table 1** Comparative study with the already reported oxide- and sulfide-based materials

Sr. no	Composition	Overpotential	Substrate	Reference
1	ZrP <sub>2</sub> S <sub>6</sub> @ MoTe <sub>2</sub>	280 mV	Pencil graphite	[53]
2	CeO <sub>2</sub> /CoSe <sub>2</sub> hybrid	288 mV	Glassy carbon	[54]
3	RuO <sub>2</sub> /CeO <sub>2</sub>	350 mV	Glassy carbon	[55]
4	Ni <sub>3</sub> Se <sub>2</sub> -Au	270 mV	Glassy carbon	[56]
5	LaNi <sub>1-x</sub> Fe <sub>x</sub> O <sub>3</sub>	439 mV	Graphite sheet	[57]
6	Ru-NiFe-P	242 mV	Nickel Foam	[58]
7	W-NiCoP	330 mV	Nikel foam	[59]
8	La-doped CuO	320 mV	Stainless steel	[60]
9	Co-doped RuO	169 mV	Glass carbon	[61]
<b>10</b>	<b>La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub></b>	<b>280 mV</b>	<b>Stainless steel</b>	<b>This work</b>

## Conclusion

In the present work, the La<sub>2</sub>S<sub>3</sub>/ZrO<sub>2</sub> nanohybrid was synthesized hydrothermally in an aqueous medium, and according to the SEM findings, the La<sub>2</sub>S<sub>3</sub> nanocrystals decorated on ZrO<sub>2</sub> nanoflakes. At the same time, the X-ray photoelectron spectroscopy, EDX, and X-ray diffraction analyses revealed the elements oxidation states and the purity of the synthesized materials. The catalyst's electrochemical behavior was confirmed via LSV, EIS, and chronoamperometry, resulting in a lower overpotential of 280 mV compared to the individuals like La<sub>2</sub>S<sub>3</sub> (390 mV) and ZrO<sub>2</sub> (420 mV) because the nanocomposite has the most active sites due to higher surface area. The fabricated material also retained its stability after 30 h. It has the potential to be employed in electrochemical water splitting in the future due to its improved performance. As a result of this novel technique, chalcogenides open an advanced avenue for OER performance, which will better tuned, and allowing for improved water splitting and, more widely, increased applicability to electrochemical and optoelectronic property domains.

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