


Cite this: *RSC Adv.*, 2022, 12, 28954

Electrocatalytic water oxidation on CuO–Cu₂O modulated cobalt-manganese layered double hydroxide†

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Layered double hydroxides (LDH) are potential electrocatalysts to address the sluggish oxygen evolution reaction (OER) of water splitting. In this work, copper oxide (CuO/Cu₂O) nanoparticles are integrated with cobalt-manganese layered double hydroxide (CoMn-LDH) to enhance their performance towards OER. The catalyst is synthesized by growing CoMn-LDH nanosheets in the presence of CuO/Cu₂O nanoparticles that were obtained by the calcination of the copper containing metal-organic framework (HKUST-1). The synthesized CoMn-LDH@CuO/Cu₂O electrocatalyst shows excellent activity towards OER with an overpotential of 297 mV at a catalytic current density of 10 mA cm⁻² and have a Tafel slope value of 89 mV dec⁻¹. Moreover, a slight decrease in the performance parameters is observed until the 15 h of continuous operation. We propose that the conductive strength of CuO/Cu₂O and its synergistic effect with the CoMn-LDH are responsible for the improved OER performance of the desired electrocatalyst.

Received 11th August 2022

Accepted 4th October 2022

DOI: 10.1039/d2ra05036f

rsc.li/rsc-advances

1. Introduction

In pursuit of clean and economical energy technologies, the water splitting reaction is of prime importance. The two half reactions of water splitting are oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Compared to HER, OER needs more attention due to its slow kinetics.¹ Commercial OER electrocatalysts are precious metal containing nanomaterials such as, Pt/C, RuO₂, and IrO₂.^{2,3} High cost and less stability under certain conditions are some of the problems associated with these catalysts.^{2,4} So, development of an efficient electrocatalyst with high activity, long-term stability, and relatively low cost, for renewable energy devices is crucial for practical applications.

Transition metal containing layered double hydroxides (LDHs) have recently shown their potential as electrocatalysts for water splitting in alkaline media.^{5,6} LDHs have a general formula of [M^{II}_{1-x}M^{III}_x(OH)₂]^{x+}[Aⁿ⁻_{x/n}·yH₂O]^{x-}, where M = metal cations coordinated to hydroxide anions, whilst Aⁿ⁻ anions are present between the LDH layers.^{7,8} In recent

literature, various LDH composites have shown considerable electrocatalytic performance for the OER process; these include FeNi-LDH,⁹⁻¹¹ NiCo-LDH,^{12,13} CoFe-LDH,¹⁴ ZnFe-LDH,¹⁵ and NiCoFe-LDH.¹⁶ It has been reported that individual LDHs structures have limited electrocatalytic performance due to the lack of exposed active sites and insufficient electrical conductivity.⁷ To address this problem, integration of LDH with the conductive substrate such as carbon fiber, Vulcan carbon, carbon nanotubes, multi walled carbon nanotubes, carbon quantum dots, and nickel foam has been widely utilized to enhance their electrocatalytic performance.¹⁷⁻²²

Previously, we have reported that copper based metal-organic framework, MOF (HKUST-1) can be converted into copper oxides (CuO/Cu₂O) under certain reaction conditions.²³ Such nanosized copper oxides have unique properties in terms of their particle size, surface area and conductivity. Many researchers also utilized copper oxides as an aid to electrocatalyst to enhance its efficiency. For instance, Niu *et al.* reported a porous carbon supported Cu/CuO nanoparticles for nitrophenol reduction, synthesized *via* calcination of a copper MOF.²⁴ The Cu/ZnO catalyst was synthesized by Zheng *et al.* *via* calcination of Cu–Zn MOF under reducing environment.²⁵ Cu/ZnO catalyst synthesized by using MOF-derived methodology was more active and stable than Cu/ZnO synthesized by other techniques. Peng *et al.* compared CuO produced through pyrolysis of HKUST-1 (CuO-p) and CuO obtained *via* co-precipitation (CuO-c).²⁶ It was concluded that CuO-p was more catalytically active than CuO-c for selective catalytic reduction (SCR) of NO. From these reports, we anticipated that the *in situ*.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2ra05036f>



Controlled growth of LDHs on the MOF-derived metal-oxides may lead to enhance the OER activity due to the combination of inherited features of both materials.

Herein, we report a novel cobalt-manganese layered double hydroxide (CoMn-LDH), synthesized in the presence of copper-based metal-organic framework, $C_{18}H_6Cu_3O_{12}$, (KHUST-1) derived CuO/Cu₂O nanoparticles to form CoMn-LDH@CuO/Cu₂O. This composite has shown promising OER activity which is superior to the commercial Pt/Ir based catalysts. The production of ultrathin nanosheets of highly OER active CoMn-LDH structure and its interaction with CuO/Cu₂O, which form an interconnected electrically conducting network, are the important aspects of this composite.

2. Experimental

2.1 Synthesis of CuO/Cu₂O

HKUST-1 was synthesized using a modified technique previously described by Wang *et al.*²⁷ The solution A was made by dissolving 0.84 g of benzene tricarboxylic acid (BTC) in 24 mL ethanol. The solution B was prepared by dissolving 1.75 g of Cu(NO₃)₂·6H₂O in 24 mL deionized water, and vigorously stirred. After that, both the solutions (A & B) were mixed and transferred to a Teflon-lined autoclave. The autoclave was kept in an oven at 120 °C for 12 h, and then allowed to cool down to room temperature. Blue colored HKUST-1 crystals were filtered and washed several times with ethanol and deionized water and dried overnight at 80 °C. The synthesized HKUST-1 was then calcined at 900 °C for 3 h in an oxygen environment to produce CuO/Cu₂O particles.

2.2 Synthesis of CoMn-LDH@CuO/Cu₂O

The composite CoMn-LDH@CuO/Cu₂O was synthesized using a hydrothermal method. Typically, 100 mg of prepared CuO/Cu₂O was completely dispersed in 15 mL of deionized water. The precursors of CoMn-LDH *i.e.*, 218 mg of Co(NO₃)₂·6H₂O, 297 mg of MnCl₄·4H₂O and 180 mg of Urea was added in above solution and stirred for 3 h. After that, the solution was transferred to a Teflon lined autoclave and heated at 130 °C for 24 h. The precipitates produced were centrifuged, washed several times with deionized water and dried at 60 °C in a drying oven.

2.3 Electrochemical measurements

All electrochemical experiments were performed at room temperature using a Gamry Interface 5000E electrochemical potentiostat configured with the prepared catalyst as the working electrode, Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. Prior to performing electrochemical tests, 1 M KOH alkaline electrolyte was purged with N₂ gas for 30 min.^{28,29} Chronoamperometry measurements were used to determine the long-term stability, and linear sweep voltammetry (LSV) experiments were carried out to investigate the current density/overpotential performance parameters at a scan rate of 50 mV s⁻¹. Impedance (EIS) experiments in 1 M KOH were carried out across a frequency range of 0.01 Hz to 100 kHz. To calibrate the reference electrode (Ag/AgCl) and

converted to RHE, the following equation was used: $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.059 \text{ PH}$.³⁰ Characterization details are in ESI.†

3. Results and discussion

To investigate the lattice parameters of the synthesized catalysts, powder X-ray Diffraction (pXRD) patterns were taken. Fig. 1 showed the characteristic diffraction peaks at 11.54°, 23.76°, and 33.5°, which confirmed the layered morphology and could be indexed to the (003), (006) and (009) planes of LDHs (JCPDS # 01-089-0460).³¹ The diffraction peaks at 2θ angles of 35.6°, 38.9°, 48.8°, 53.7°, 58.6°, 61.9°, 65.6°, 67.8°, correspond to the indices (002), (111), (−202), (020), (202), (−113), (−311) and (220) reflections of CuO lattice planes, respectively (JCPDS # 00-002-1040).³² The diffraction peaks at 36.6°, 42.5° and 73.4° are attributed to the (111), (200) and (311) lattice planes of Cu₂O, respectively (JCPDS # 00-001-1142). The intensity of the typical diffraction peaks of Cu₂O (111) and CuO (111) planes shows that CuO is the predominant specie produced, with traces of Cu₂O.^{33–35} The pXRD pattern of CoMn-LDH@CuO/Cu₂O have all the characteristics peaks of CoMn-LDH and MOF derived CuO/Cu₂O which reveals that dispersion of CuO/Cu₂O does not change the chemical composition of the catalyst.

The surface elemental composition was confirmed by the XPS analysis. Fig. 2a shows two peaks at 781.6 eV and 798.2 eV correspond to the binding energies (BEs) of Co 2p_{3/2} and Co 2p_{1/2}, respectively, and two satellite peaks at 786.8 eV and 803.4 eV were also observed. The value of Co 2p_{3/2} is distinct from Co⁰ (777.6 ± 0.8 eV) but near to Co²⁺ (780.9 ± 0.4 eV), suggesting that the valence state of cobalt is Co²⁺. Mixed oxidation states of Mn have been observed. The binding energy values of 641.4 eV, 642.8 eV and 644.7 eV correspond to Mn²⁺, Mn³⁺ and Mn⁴⁺, respectively. Mn 2p_{1/2} has peaks at 647.3 eV (Fig. 2b). Cu 2p_{3/2} and Cu 2p_{1/2} binding energies have two main peaks at 933.8 eV and 953.5 eV, respectively, with spin-orbit splitting of around

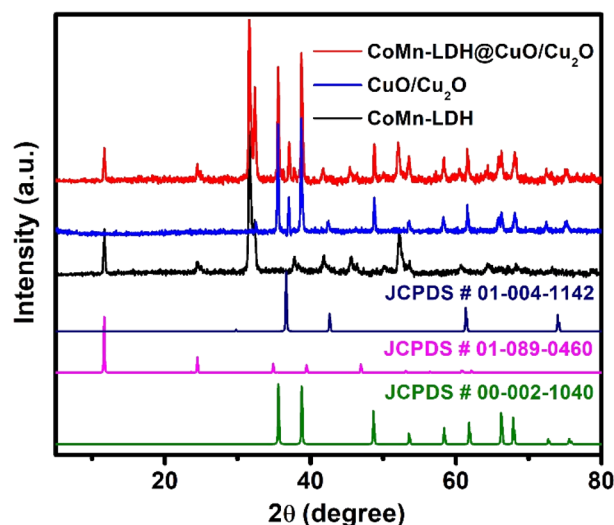


Fig. 1 Comparison of powder XRD patterns of CoMn-LDH, CuO/Cu₂O and CoMn-LDH@CuO/Cu₂O.

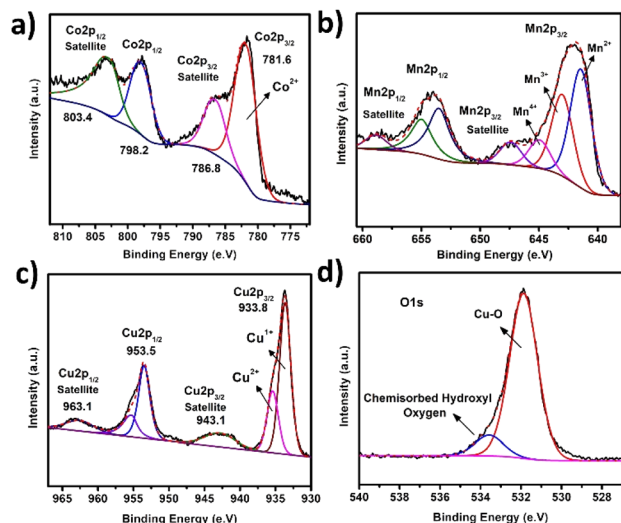


Fig. 2 XPS spectra of CoMn-LDH@CuO/Cu₂O; (a) Co 2p (b) Mn 2p (c) Cu 2p (d) O 1s.

20.2 eV. The appearance of two satellite peaks at higher binding energies than the Cu 2p_{3/2} and Cu 2p_{1/2} peaks and shoulder peak of Co 2p_{3/2} suggests the presence of Cu²⁺ and Cu¹⁺ states. Deconvolution of the O 1s peak results in the formation of two sub peaks: 'O' in CuO (532.3 eV) and 'O' in chemisorbed hydroxyl group (533.5 eV) (Fig. 2d).

The size, morphology and structure of the resulting materials were characterized by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The interior structure of as synthesized CoMn-LDH and composite CoMn-LDH@CuO/Cu₂O is examined by the high resolution transmission electron microscope (HRTEM). In Fig. 3a and c SEM and TEM results of CoMn-LDH shows

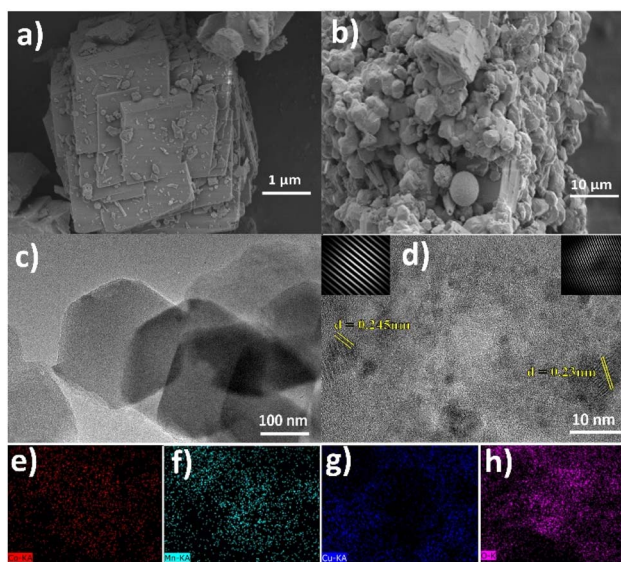


Fig. 3 SEM and TEM images of CoMn-LDH (a and c), CoMn-LDH@CuO/Cu₂O (b and d), elemental mapping images of cobalt (e), manganese (f), copper (g), oxygen (h).

hexagonal platelets which further confirms the layered structure of CoMn-LDH.³¹

Fig. 3b and d shows SEM and HRTEM images of composite CoMn-LDH@CuO/Cu₂O revealing the full dispersion of Cu-BTC derived CuO/Cu₂O across the layers of LDH. This dispersion facilitates mass and charge transfer which results in high ECSA. Lattice fringes can also be seen in Fig. 3d with the *d*-spacing (*d* = 0.23 nm) and (*d* = 0.245 nm) which correspond to (111) plane of CuO and (111) plane of Cu₂O respectively in XRD spectra of CuO/Cu₂O.^{31,33,35} The energy dispersive X-ray spectroscopic analysis shown in (Fig. S2†) and elemental mapping shown in Fig. 3e–h indicates the uniform distribution of Co, Mn, Cu and O elements, thus confirming the formation of CoMn-LDH@CuO/Cu₂O.

3.1 Oxygen evolution reaction studies

All the electrochemical studies were carried out in 1 M N₂-saturated KOH solution, the catalytic performance of the CoMn-LDH@CuO/Cu₂O were investigated using a three-electrode system. To provide a fair comparison, the mass loading of the CoMn-LDH@CuO/Cu₂O catalyst was set to the same value as that of the CoMn-LDH and CuO/Cu₂O samples (1 mg cm^{−2}). The linear sweep voltammetry (LSV) curves of catalysts *versus* reversible hydrogen electrode (RHE) for OER without IR correction are shown in Fig. 4a. As predicted, in 1 M KOH solution, the bare electrode exhibits negligible OER activity. Among all the three synthesized electrocatalysts, the CoMn-LDH@CuO/Cu₂O exhibits the lowest onset potential for OER and the highest current density at the same overpotential, indicating the highest electrochemical activity towards water oxidation. The current density of 10 and 20 mA cm^{−2} was achieved by the CoMn-LDH@CuO/Cu₂O at an overpotential of 297 mV and 320 mV respectively, which is far less than CoMn-LDH (380 mV) and CuO/Cu₂O (540 mV) at the same current density. For comparison OER activity of RuO₂ was also checked under same circumstances and it required overpotential of 320 mV@10 mA cm^{−2}. Indeed, when compared to previously reported electrocatalysts, CoMn-LDH@CuO/Cu₂O shows superior OER activity. As shown in Fig. 4b the Tafel slope was calculated to check the kinetics of the reaction and CoMn-LDH@CuO/Cu₂O exhibits low value of Tafel slope of 89 mV dec^{−1}, as compared to 97 mV dec^{−1} for RuO₂, 190 mV dec^{−1} for CuO/Cu₂O and 160 mV dec^{−1} for CoMn-LDH. We computed turnover frequency (TOF), another essential parameter, to assess the intrinsic characteristic of the electrocatalyst. The TOF value of CoMn-LDH@CuO/Cu₂O is (0.012 s^{−1}) at onset overpotential.

The electrochemical surface area (ECSA) of an electrocatalyst is a critical parameter because it determines the extent to which active sites for positive/negative ions are exposed to the electrode surface when anodic/cathodic potentials are applied solely in the non-faradaic region. The area of exposed active sites is directly related to double layer capacitance (Cdl) of modified working electrode. To determine the capacitance of the double layer, we used cyclic voltammetry in the non-faradaic region at various scan rates. Cyclic voltammograms shown in Fig. 4c, demonstrates increase in current density with the



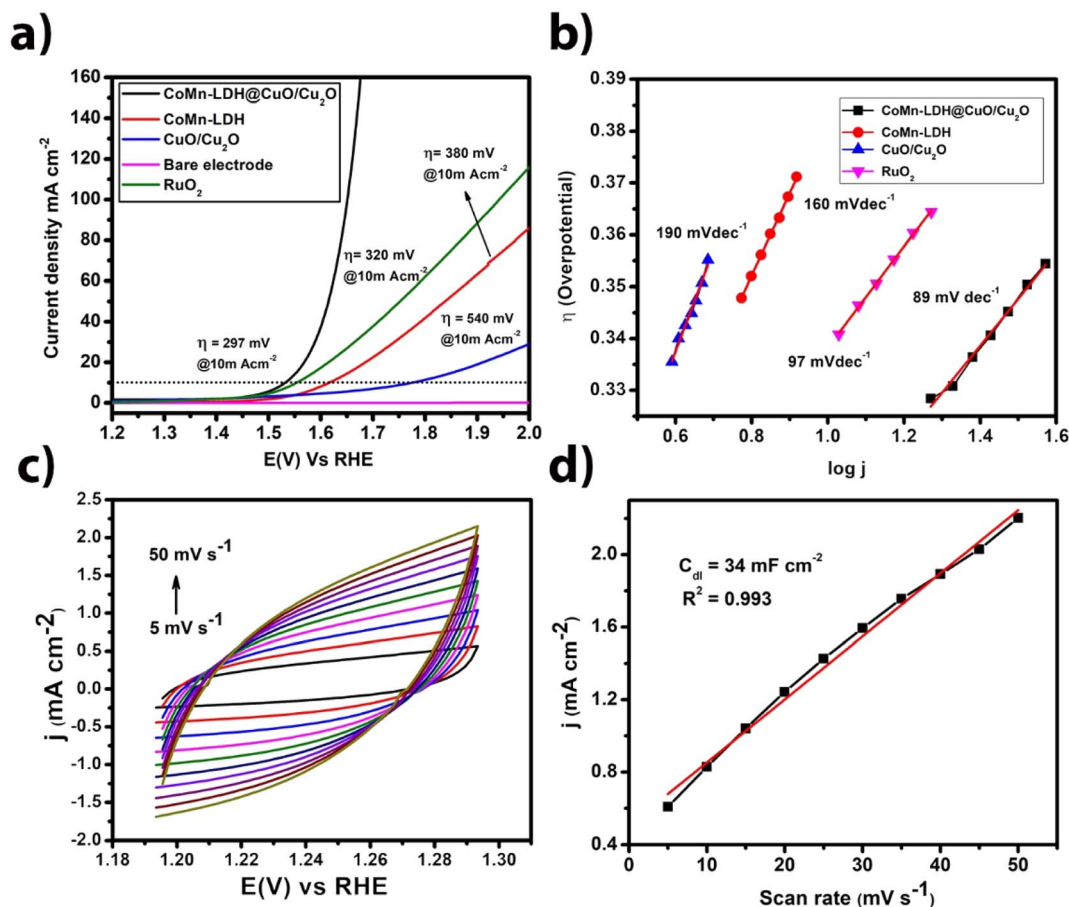


Fig. 4 (a) Linear sweep voltammograms of CoMn-LDH, CuO/Cu₂O, CoMn-LDH@CuO/Cu₂O, RuO₂ and Bare electrode (b) Tafel slopes of CoMn-LDH, CuO/Cu₂O, CoMn-LDH@CuO/Cu₂O and RuO₂ (c) non-faradaic region cyclic voltammograms at various scan rates (d) anodic current density plot vs. scan rate of CoMn-LDH@CuO/Cu₂O fabricated electrode in 1 M KOH solution as an electrolyte.

increase in the scan rate. A single potential value was computed by detecting it in the capacitive potential window that is non-Faradic. In the region of 5 to 50 mV s⁻¹, plotting anodic current *versus* scan rates yielded a straight line whose slope is equal to C_{dl}. The C_{dl} values were calculated for CoMn-LDH@CuO/Cu₂O (34 mF cm⁻²), CoMn-LDH (14.4 mF cm⁻²) and CuO/Cu₂O (9.2 mF cm⁻²) (Fig. S6†). It was observed that CoMn-LDH@CuO/Cu₂O had the highest value of double layer capacitance which indicates high electrochemical active surface area (ECSA). The double layer capacitance values of some reported materials also support our C_{dl} studies *i.e.* NiCo-P/C nanocubes (145 mF cm⁻²), NiCo LDH nanocubes (9.16 mF cm⁻²) and NiCo-P nanoboxes (28.94 mF cm⁻²).³⁶ The ECSA has also been calculated from double layer capacitance. We noticed that CoMn-LDH@CuO/Cu₂O exhibits highest electrochemical active surface area (425 cm²) compared to CoMn-LDH (180 cm²) and CuO/Cu₂O (115 cm²) materials. The high value of C_{dl} and ECSA indicates that CoMn-LDH@CuO/Cu₂O facilitate mass and charge transfer.

Conventionally, the electrochemical water oxidation process primarily entails three intermediate stages: (1) the adsorption of water molecule onto the electrode surface, (2) the separation of water into molecular oxygen, and (3) the evolution of oxygen.

The CoMn-LDH nanosheets have a distinct layered structure and the sheets are usually stacked on over the other. Since LDH has a wide interlayer gap, the hydroxide units and molecules of water can diffuse across the layers and move randomly, enabling close contact among the catalyst and active species. The addition of CuO/Cu₂O in the catalyst not only help in enhancing the conductivity and thus charge transfer but also to expose the active sites *via* preventing LDH sheets from coagulation. Therefore, the electrochemical active surface area increases, and reaction occur at more accessible sites. In addition, as the interlayer spacing will make it easier for O₂ to transit and to evolve from the electrode surface, which is essential for the third phase of the OER process.

As predicted by the Pourbaix diagrams of Co³⁷ and Mn,³⁸ the high-valent cations (Co^{3+/4+}, or Mn^{3+/4+}) are highly crucial for OER.³⁹ X-ray absorption spectroscopy (XAS),⁴⁰ *in situ* Raman spectroscopy,⁴¹ and density functional theory (DFT) calculations⁴² have demonstrated that Co hydroxide electrocatalysts can be oxidized *in situ* to the catalytically active CoOOH in alkaline conditions, which has been regarded as the preferred metal species for OER. The role of manganese cation on the other hand is to exchange oxygen atoms with the electrolyte at relevant potentials.⁴³ This characteristic of Mn may facilitate



OER. In alkaline media, the water oxidation reaction often comprises proton-coupled electron transfer (PCET) activities, namely the PCET transformation of Co^{3+}/OH to Co^{4+}/O , prior to the formation of molecular oxygen.⁴⁴ So, we can say that under given conditions, cobalt center is the actual active catalytic site, however, manganese center and copper oxide species are proposed to boost the OER ability of cobalt center *via* different mechanistic roles, as stated above.

Determining the faradaic efficiency of a catalyst is a beneficial parameter for elucidating its oxygen generation ability (FE). To obtain the FE, the actual and predicted yields of evolved oxygen are compared by using chronoamperometry. To check the faradaic efficiency of the catalyst, controlled potential electrolysis technique (CPE) was performed utilizing comparable electrochemical reaction conditions at a static potential of 1.45 V *versus* RHE for a period of 1 h.⁴⁵ To establish a baseline, DO meter probe was immersed in an electrolyte of airtight anodic chamber and the concentration of dissolved oxygen was measured for an hour. The expected yield of O_2 was estimated using Faraday's law and the charge stored during the electrochemical reaction. The faradaic efficiency was computed through the actual and theoretical yield for CoMn-LDH@CuO/Cu₂O (92.4%), CoMn-LDH (75.6%), and CuO/Cu₂O (62.3%) (Fig. S1 and Table S1†). The current due to the redox reaction of metals is also involved along with water electrolysis.

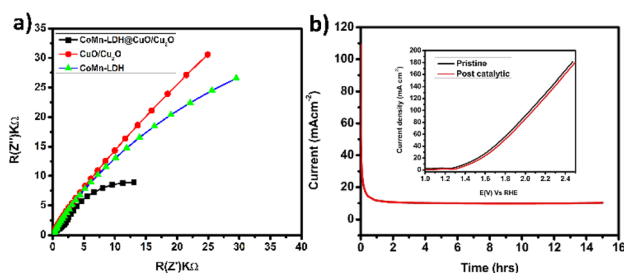


Fig. 5 (a) EIS spectra of CoMn-LDH, CuO/Cu₂O, CoMn-LDH@CuO/Cu₂O between the range of 0.1 Hz and 100 kHz. (b) Controlled potential electrolysis of CoMn-LDH@CuO/Cu₂O for 15 h (inset) LSV curve of pristine and post catalytic CoMn-LDH@CuO/Cu₂O.

Electrochemical impedance spectroscopy was used to evaluate the conductivities of CoMn-LDH, CuO/Cu₂O, and CoMn-LDH@CuO/Cu₂O composite between 0.1 Hz and 100 kHz. The charge transfer resistance (R_{ct}) is related with the semicircle diameter in the Nyquist plot's high frequency region, and a small R_{ct} value indicates a quick reaction rate. In Fig. 5a it can be clearly shown that CoMn-LDH@CuO/Cu₂O has small radii of its semi-circle and low resistance to charge transfer (R_{ct}) as compared to individual CoMn-LDH and CuO/Cu₂O, thus revealing its fast OER kinetics and low charge transfer resistance. The low charge transfer resistance, which facilitates efficient charge transport, is owing in part to the dispersion of CuO/Cu₂O and the synergistic impact of the presence of several transition metals, as well as other intrinsic factors. For commercial and industrial water electrolyzer, the stability of catalyst is a critical criterion. Since catalyst's catalytic activity and selectivity are the key parameters, its effectiveness is critical unless it exhibits adequate long-term stability. For this purpose, a 15 h controlled-potential electrolysis (CPE) study was conducted under constant experimental conditions utilizing chronoamperometry at 1.42 V *against* RHE to determine the stability and durability of the catalyst CoMn-LDH@CuO/Cu₂O. A steady current of 10 mA was maintained by the catalyst until the last minute (Fig. 5b). Linear sweep voltammetry has been performed to check the durability of the catalyst. From the inset of Fig. 5b it is cleared that the onset potential and maximum current density values of the LSV of modified electrode (CoMn-LDH@CuO/Cu₂O) that has been coated (pristine and post-catalytic reactions) showed no significant change, indicating that structure of CoMn-LDH@CuO/Cu₂O remained the same throughout the catalytic phenomena. XPS analysis of the post catalytic sample has also been performed. There is no significant change observed which indicates that catalyst's structure and physical properties are retained after CPE test of 15 h (Fig. S3–S5†). Table 1 shows the comparative analysis of the as prepared anode with previously reported composites of LDHs. The most probable proposed mechanism for oxygen evolution reaction in alkaline media is shown in Fig. S6.† In the first step metal active site bind with OH[−] ion from water to form M-OH. Further oxidation leads to the formation of M-O specie

Table 1 Comparative analysis of the OER efficiency of CoMn-LDH@CuO/Cu₂O with the reported composites of layered double hydroxide

Catalyst	Method	Overpotential at 10 mA cm ^{−2} (mV)	Ref.
Fabrication of CoFe-LDH over graphitic nitrides	Co-precipitation	280	46
NiFeMn-LDH	Hydrothermal	289	47
Co @ NiFe-LDH	Hydrothermal	267	48
Co intake Fe Ni-LDH	Hydrothermal	220	49
Al @ NiFe-LDH	Solvothermal	300	50
NiMn-LDH@MWCNT	Refluxing	350	51
Ni Fe-LDH on carbon quantum	Solvothermal	235	21
CoFe-LDH @ Cu foam	Electrodeposition	240	52
CoFe-LDH	Hydrothermal	266	53
Enriching vacancy CoFe-LDH	Acid Etching	302	54
CoFe-LDH@g-C ₃ N ₄	Hydrothermal	322	55
CoMn-LDH@MWCNT	Refluxing	300	51
CoMn-LDH@CuO/Cu ₂ O	Hydrothermal	297	This work



followed by M-OOH which is thermodynamically unfavorable intermediate because of the weak interaction between metal and -OOH. In the last step metal oxygen bond breaks leading to the formation of O₂. The comparative study of various reported catalysts with the CoMn-LDH@CuO/Cu₂O is shown in Table 1.

4 Conclusions

In conclusion, CoMn-LDH@CuO/Cu₂O was successfully fabricated by a simple and facile process. CuO/Cu₂O nanoparticles produced by the calcination of HKUST-1 were added during the growth of CoMn-LDH nanosheets and their integration is proved using PXRD, SEM, TEM, EDX and XPS techniques. The desired electrocatalyst exhibits High performance OER activity. To drive a current density of 10 mA cm⁻², the optimized anode only requires an overpotential of 297 mV with the Tafel slope value (89 mV dec⁻¹) which is remarkably lower than the individual CoMn-LDH and CuO/Cu₂O. Additionally, our catalyst displays high stability for OER with negligible current loss during a 15 h period. Our experimental results indicates that the interaction of CoMn-LDH and CuO/Cu₂O increased the electrochemical active surface area and decreased the charge transfer resistance, both of which contribute to the excellent OER performance of the catalyst.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work was financially supported by the Pakistan Academy of Sciences (PAS) and Higher Education Commission (HEC) of Pakistan (No. 8400/Federal/NRPU/R&D/HEC/2017).

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