1. Introduction

Fossil fuels are diminishing resources that contribute notably to environmental pollution, so developing sustainable energy sources suitable for our growing energy requirements is critical for the survival of humankind. An abiotic component of promising renewable energy infrastructure with no reliance on fossil fuels and no carbon dioxide emission is the splitting of water into hydrogen and oxygen. In photoelectrochemical (PEC) water splitting, solar energy is directly converted to fuel by light-absorbing semiconductors. As a new generation energy carrier, solar hydrogen will play an important role in our lives because it is storable, transportable, and convertible into efficient electricity in fuel cells, as well as being a viable and clean source of power due to its extraordinarily high energy density. During water splitting, the reductive half-reaction with a two-electron transfer mechanism is relatively easier than the oxidative half-reaction involving a four-electron transfer mechanism, which is the most energy-intensive step in the overall water splitting process. Therefore, the slow kinetics of the oxygen evolution reaction, OER, requires a substantial overpotential to generate measurable current densities. A large positive change in Gibbs free energy ($\Delta G^0 = 237.13$ kJ mol$^{-1}$) causes the full water splitting reaction to be thermodynamically an uphill reaction. From this perspective, it is challenging to design highly effective photocatalysts while considering crucial parameters in the development of suitable semiconductors. These parameters include band gap width, optical absorption edge, stability against photodegradation/lifetime, solar photons to current efficiency, cost-effectiveness, catalytic activity and surface structure. Furthermore, a high degree of crystallinity, i.e. a smaller amount of defects, is often required for water splitting because recombination between photogenerated carriers is particularly a serious problem in uphill reactions. Beginning with the discovery of Fujishima and Honda in the early 1970s, metal oxide or mixed-metal oxide semiconductors have been well studied as water splitting photoanodes due to their low cost and high stability in aqueous environments. Because the mixture of two metals in an oxide matrix can generate materials with unique chemical and physical properties, much consideration has been paid to the mixed-metal oxides, such as metal titanates, metal tungstates and metal molybdates.

Moreover, the growing $CO_2$ emission is an inevitable result of fossil fuels consumption because of the accessibility, diversity and high energy density of these fuels. However, the ever-increasing use of fossil fuels will cause dependence on them despite their limited reserves; additionally, global warming, drastic environmental changes and an intense threat to human survival are other issues associated with the use of fossil fuels. To resolve these issues, the best approach is to convert $CO_2$ into carbon-containing fuels as a renewable energy resource. Recently, electrochemical reduction of accumulative $CO_2$ has been considered as a feasible strategy for the conversion and utilization of this gas. This process was reported for the first time in the late 1970s and has been followed by studies to identify suitable materials and develop appropriate techniques to efficiently reduce $CO_2$ to hydrocarbons. In this regard, bifunctional electrocatalysts have been developed for overall water splitting and $CO_2$ reduction. Overall water splitting and $CO_2$ reduction are two very important reactions from the environmental viewpoint. The former produces hydrogen as a clean fuel and the latter decreases the amount of $CO_2$ emissions and thus reduces greenhouse effects. Here, we prepare two types of copper molybdate, $CuMoO_4$ and $Cu_2Mo_2O_9$, and electrochemically investigate them for water splitting and $CO_2$ reduction. Our findings show that $Cu_2Mo_2O_9$ is a better electrocatalyst for full water splitting compared to $CuMoO_4$. It provides overpotentials, which are smaller than the overpotentials of $CuMoO_4$ by around 0.14 V at a current density of 1 mA cm$^{-2}$ and 0.10 V at −0.4 mA cm$^{-2}$, for water oxidation and hydrogen evolution reactions, respectively. However, $CuMoO_4$ adsorbs $CO_2$ and the reduced intermediates/products more strongly than $Cu_2Mo_2O_9$. Such different behaviors of these electrocatalysts can be attributed to their different unit cells.

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Our findings show that $Cu_2Mo_2O_9$ is a better electrocatalyst for full water splitting compared to $CuMoO_4$. It provides overpotentials, which are smaller than the overpotentials of $CuMoO_4$ by around 0.14 V at a current density of 1 mA cm$^{-2}$ and 0.10 V at −0.4 mA cm$^{-2}$, for water oxidation and hydrogen evolution reactions, respectively. However, $CuMoO_4$ adsorbs $CO_2$ and the reduced intermediates/products more strongly than $Cu_2Mo_2O_9$. Such different behaviors of these electrocatalysts can be attributed to their different unit cells.

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time by Sir B. C. Brodie in 1873 and later in the 1990s by Hori et al.\textsuperscript{15,16} However, many efforts have been carried out to overcome usual challenges, such as poor efficiency because of kinetic barrier for stable molecules, weak selectivity resulting from reduction products competition, side reactions and hydrogen evolution reaction (HER).\textsuperscript{17,18} Therefore, probing new electrocatalysts that efficiently reduce CO\textsubscript{2} into liquid fuels, especially in mild conditions, is extremely significant. For this purpose, copper (Cu) and Cu-based electrodes have been investigated as electrocatalyst candidates due to their intrinsic catalytic activity and variation of reduction products, which considerably depend on surface properties and morphology.\textsuperscript{19–20}

Despite many experimental efforts and computational calculations, the mechanism of CO\textsubscript{2} reduction on Cu electrodes is intricate and the exact reaction path is controversial.\textsuperscript{21,22}

With regard to the above studies, it seems that Cu-based mixed oxides can be considered as bifunctional-electrocatalysts, which can electrochemically oxidize water and reduce CO\textsubscript{2}. For example, some of the widely studied copper-based photocatalysts for water splitting have been crystalline copper phosphate nanosheet,\textsuperscript{31} cuprous oxide composites,\textsuperscript{34–36} copper(II) tungstate\textsuperscript{37–39} and copper(II) borate.\textsuperscript{40} More recently, scientists have tried to find nanomaterials that exhibit remarkable properties to catalyze both hydrogen production and water oxidation reactions when the applied potentials fluctuate between oxidative and reductive conditions in the same reaction electrolyte.\textsuperscript{41} A copper-based catalyst composite film was found to be an interesting electrocatalyst for both HER and OER in the same electrolyte.\textsuperscript{42}

To the best of our knowledge, there is no report on the application of copper molybdates for these properties. However, over the past several years, different preparations and structures of transition metal molybdates have been widely reported; these include doped,\textsuperscript{43,44} layered,\textsuperscript{45–47} nanosheet,\textsuperscript{48,49} powder,\textsuperscript{50} flower-like,\textsuperscript{51} nanoplate\textsuperscript{52} and micropompoms\textsuperscript{53} structures. These structures are widely used in the areas of catalysis, magnetic application and energy storage. Furthermore, CuMoO\textsubscript{4} is a thermochromic, trisochromic and piezochromic material, so it can be used in pressure and/or temperature sensors. Recently, extensive studies have been conducted on using transition metal molybdates in catalysis/photocatalysis,\textsuperscript{44,49,53–55} magnetic applications\textsuperscript{56–58} and lithium batteries;\textsuperscript{52} for example, preparation of hybrid Cu\textsubscript{2}O/CuMoO\textsubscript{4} nanosheet electrodes for high-performance asymmetric supercapacitors,\textsuperscript{48} Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9} nanoplates with excellent lithium storage performance\textsuperscript{52} and Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9} micropompoms with excellent performance in photocatalytic degradation of Congo red under visible light, photocurrent response and lithium storage.\textsuperscript{53} Two different compounds of copper molybdate exist with two different chemical formulae of CuMoO\textsubscript{4} and Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9}. Both of them contain MoO\textsubscript{4} tetrahedra, CuO\textsubscript{4} octahedra and CuO\textsubscript{2} pyramid units. In CuMoO\textsubscript{4}, six copper-oxygen polyhedra share edges to form a spiral-shaped chain fragment, interconnected by MoO\textsubscript{4} tetrahedra,\textsuperscript{54} whereas sharing the edge oxygen atoms of Cu-based polyhedra makes a zigzag ribbon.\textsuperscript{55}

The crystal structures of both compounds are shown in Fig. 1; these structures were reproduced by Mercury software.\textsuperscript{56–61}

from the Cambridge Crystallographic Data Center, using their CIF files. Recently, we reported that tungstate-derived copper has a good activity for electrochemical reduction of CO\textsubscript{2},\textsuperscript{62} so it is expected here that we have molybdate-derived copper from two different sources, CuMoO\textsubscript{4} and Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9}, with two different distribution of copper atoms and consequently different activities.

Due to these different crystal structures, their comparative study as bifunctional catalysts for electrochemical water splitting and CO\textsubscript{2} reduction seems very interesting. In this study, we successfully prepare, characterize and electrochemically investigate both nano-CuMoO\textsubscript{4} and nano-Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9} structures.

2. Experimental

2.1. Materials preparation

The reactions were carried out under air at room pressure. High purity (>99%) AR grade copper nitrate Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, sodium molybdate Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O, citric acid and ammonium heptamolybdate, (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O were obtained from commercial sources.

For the synthesis of Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9}, 2.4195 g (0.01 mmol) Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O was dissolved in 50 mL deionized water to form a transparent solution. Then, 2.4160 g (0.01 mmol) Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O was dissolved in 10 mL deionized water to reach a dark blue solution, which was added to the first solution dropwise by a burette and stirred at room temperature for 30 min. After stirring, the beaker was subjected to 80 W cm\textsuperscript{–2} ultrasonic radiation under air for 30 min using an ultra sonicator operating at 40 kHz. The reaction was carried out in a glass balloon, which was heated in an oil bath at about 100 °C for 20 h. The balloon was connected to a reflux condenser system open to the atmosphere. Next, the resulted particles were filtered and washed several times with distilled water and ethanol and then dried in an oven at a temperature of 75 °C for 3 h. The obtained powders were treated under air at temperatures ranging from 25 °C to 400 °C for 2 h and were then remained at this temperature for 4 h. Finally, Cu\textsubscript{3}Mo\textsubscript{2}O\textsubscript{9} was prepared as a brown-orange powder.
For the preparation of CuMoO₄, 5 mL of copper nitrate solution (0.50 M) was added to molybdate solution, which was obtained by dissolving 0.4414 g ammonium heptamolybdate in 50 mL deionized water (pH = 4.7). The mixture was stirred about 15 min, and then a citric acid (CA) solution in a molar proportion of 3 : 1 CA : cation was added. By evaporating the homogeneous solution at 90 °C (low-temperature crystallization), a sky blue gel was gradually formed. The obtained gel was transferred to a highly porous Prussian blue matrix at 120 °C for 24 h; then, it was calcined over a wide range of temperatures and times as shown in Fig. 2 to optimize its surface area, crystallinity and photocatalytic activity. Finally, a green yellowish powder that was obtained at the end of the process was characterized.

2.2. Electrode fabrication

For electrochemical studies, working electrodes were prepared by the electrophoretic method. Two 1 × 5 cm² pieces of commercial stainless steel with a separation distance of 2 cm were inserted into a mixture, which was prepared by dispersing 0.0056 g of the prepared samples in 5 mL ethanol and five-minute exposure under 50 kHz ultrasonic waves. A potential of 20 V was applied between the two electrodes for 60 s. Next, the prepared electrodes were dried at 80 °C for 3 h and finally at 400 °C for 15 min.

2.3. Material characterization

XRD pattern of CuMoO₄ and Cu₃Mo₂O₉ samples were recorded on an XPERT-PRO powder X-ray diffractometer. The CuKα (k = 1.5406 and 1.5443 Å) radiation was used, and diffractions were measured over 2θ range of 5–80°. Transmission electron microscopy (TEM) images were obtained with a CM120 electron microscope from Philips. The diffuse reflectance spectra were determined with a UV-Vis spectrophotometer Avantes (Avaspec-2048-TEC) with BaSO₄ as the standard reference. The magnetic properties were measured using a vibrating sample magnetometer (VSM) system (Lake Shore 7404).

2.4. Electrochemical characterization

All electrochemical measurements on the surface of catalysts were conducted in a 0.1 M NaOH (pH = 13) solution by a standard three-electrode cell containing Ag/AgCl as the reference electrode, a platinum mesh as the auxiliary electrode and an electrophoretically deposited material electrode as the working electrode using a Solartron SI-1260 electrochemical interface. For Mott–Schottky analysis, a Solartron Phase Gain Analyzer SI1260 was used to determine electrochemical impedance spectra (EIS) by handling a frequency of 10,000 Hz, an AC voltage amplitude of 10 mV in different scanning potential ranges for the deposited electrode vs. Ag/AgCl (between −0.35 and 0.2 V for CuMoO₄, and between −0.45 and 0.4 V for Cu₃Mo₂O₉) both in the dark and under illumination by a fluorescent lamp. A range of frequencies between 0.1 and 100,000 Hz was used in EIS measurements with a 10 mV amplitude perturbation.

The electrocatalytic activities of the working electrodes were tested using Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV), at a scan rate of 10 mV s⁻¹ in different potential ranges. All electrochemical tests were performed at ambient temperature and pressure. To reduce the additional ohmic resistance, bubbles that were generated on the electrode surface under OER and HER were dispersed by stirring the solution at 1000 rpm during the reaction. Moreover, to enhance the mass transport of CO₂ during the electroreduction, CO₂ was continuously bubbled.

3. Results and discussion

3.1. XRD analysis

As shown in Fig. 3a, the XRD patterns of the as-prepared CuMoO₄ and Cu₃Mo₂O₉ samples reveal their crystalline nature, which are consisted of a single-phase and orthorhombic Cu₃Mo₂O₉ with space group Pna₂ and an orthorhombic CuMoO₄ with space group P1. As shown, the broadening of the diffraction
CuMoO₄, respectively. The average crystallite size calculated (half maxima) of the XRD peaks of Cu₃Mo₂O₉ and CuMoO₄ to (002), (140) and (131) planes of Cu₃Mo₂O₉, and at 2 to (012), (201) and (211) planes of CuMoO₄ respectively. The (002) and (012) reflection peaks were used for the calculation of the crystallite size of Cu₃Mo₂O₉ and CuMoO₄, respectively. The average crystallite size calculated using the Debye–Scherrer equation from the FWHM (full-width half maxima) of the XRD peaks of Cu₃Mo₂O₉ and CuMoO₄ samples were found to be approximately 49 and 134 nm, respectively.

3.2. TEM

TEM studies provide further insight into the nanostructure and topography of the treated samples. Fig. 3b and c shows the TEM images of Cu₃Mo₂O₉ and CuMoO₄ for the formation of rod-shaped orthorhombic and multiform shape particles of the samples; both monocrystalline particles have diameters that are in good agreement with the size obtained from powder XRD. The nanoparticles are a little agglomerated.

3.3. Magnetic properties analysis

The relationships between the magnetization (M) and magnetic field (H) of Cu₃Mo₂O₉ and CuMoO₄ nanoparticles was determined by a vibrating sample magnetometer (VSM) system (Lake Shore 7404). Fig. 4a shows the M–H curve in the range from −18 to 18 kG with a saturated magnetization. A linear increment above 7 kG with a narrow hysteresis loop occurs between −2 and 2 kG; this pattern is the characteristic of both ferromagnetic and antiferromagnetic interactions for both samples. 65,66

3.4. Optical properties

The optical properties of the samples were measured by UV-Vis DRS spectrum. Fig. 4b demonstrates the DRS spectra of the prepared Cu₃Mo₂O₉ and CuMoO₄ samples. Two sequential absorption bands can be identified in these samples. One band is located above 600 nm, and the other one below 600 nm; these results are in good agreement with the color of the samples. The former can be mainly attributed to d–d transition of Cu²⁺ ions (3d⁸), whereas the latter may be due to the Cu(3d) ← O(2p) LMCT or Mo(4d) ← O(2p) LMCT and an Mo(4d) ← Cu(3d) MMCT, which is located at wavelengths higher than LMCT band. 66,67

The direct and indirect optical band gaps of nanoparticles were extracted according to Tauc’s equation. 68,69 According to Tauc’s equation, the relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as:

\[
(αhν)^{1/n} = A(hν - E_g)
\]  

(1)

where A is a constant, \(E_g\) is the band gap energy of the materials; the exponent n depends on the transition type and is equal to 0.5 and 2 for direct and indirect transitions, respectively. 70 To determine the possible transitions, \((αhν)^{1/n}\) was plotted versus hν, and the corresponding band gaps were obtained by extrapolating the steepest part of the graph on the hν axis for \((αhν)^{1/n} = 0\). The direct and indirect band gap energies were obtained from, respectively, \((αhν)^{2}\) and \((αhν)^{1/2}\) vs. hν as shown in Fig. S1.†

The larger band gaps of both samples correspond to the direct electronic transition between the upper edge of O:2p valence band and the lower edge of Mo:4d conduction band. The calculated band gaps for these transitions are 2.4 and 2.6 eV for Cu₃Mo₂O₉ and CuMoO₄, respectively. The lower energy indirect transitions can be explained by assuming the existence of narrow band correlated-electron states in the band gap instead of a single wide band of uncorrelated-electron states that may correspond to Cu²⁺:3d⁸ band. We speculate that in addition to the contribution of Cu (3d) on the top of O (2p) valence band, the conduction band of both samples contain Cu (3d) characteristic, in agreement with our experimental observations. The Jahn–Teller distortion of Cu²⁺ gives rise to a d-orbital splitting in which the degeneracy of σ-antibonding orbitals is broken. 98 The calculated Tauc’s plot indirect band gaps are 2.1 and 2.3 eV for Cu₃Mo₂O₉ and CuMoO₄ samples, respectively, so their absorption edges are in the visible range of the spectrum. Ansari et al. reported that the electronic
transitions of CuMoO₄ are of indirect type and a band gap of 3.06 eV was obtained,²⁷ whereas values of 2.38, 2.80 and 2.15 eVs were obtained by other researchers.²⁵–²⁷ Moreover, Dutta et al. found an indirect band gap of 2.32 eV.²⁴

3.5. Mott–Schottky analysis

For Mott–Schottky analysis, one has to select a range of potentials in which Faraday’s reaction does not occur. To determine this range, cyclic voltammetric technique was used. The characteristic of Faraday’s processes is the evolution of peaks in cyclic voltammograms. For non-faradic or capacitive processes, no peak is observed and the voltammogram is almost rectangular. Cyclic voltammograms with a scan rate of 10 mV s⁻¹ in potential ranges between 0.2 and −0.35 for CuMoO₄ and between 0.25 and −0.45 V for Cu₃Mo₂O₉ in 0.1 M NaOH were obtained. In this way, a range of potentials was determined over which the cyclic voltammograms showed no faradic current, and only a capacitive current was observed. In order to ensure that the observed behavior in the voltammograms was capacitive, the effect of different scan rates on the voltammograms was evaluated. If the observed behavior is capacitive, the anodic and cathodic currents should increase with increasing the scan rate. Therefore, the performance of samples in these potential regions can be considered as capacitive, as shown in Fig. S2.†

When a semiconductor is exposed to an electrolyte, it reaches the thermodynamic equilibrium with the electrolyte by exchanging electrons through the interface and adjusting the Fermi level of the semiconductor to the Fermi level of the electrolyte, which results in the formation of a space charge layer. The Fermi level position of the electrolyte is constant because the number of available states in the electrolyte solution is typically more than the number of states in the semiconductor. With regard to electron transfer from/to a semiconductor to/from an electrolyte, an excess of immobilized charge in the semiconductor and an excess of opposite charge in the electrolyte are produced just behind the interface and in the space charge layer. This implies that the energy bands are bent,²⁵ and the amount of bending depends on the difference between band edge energy in the semiconductor and at the interface; furthermore, the amount of bending corresponds to the potential drop in the space charge layer, Uₛ. When an external electrical source is applied, then Uₛ = Uₜₚ − Uᵥᵣᵦ, where Uᵥᵣᵦ is the flat band potential, that is, a unique potential for which the potential drop between the bulk and surface is zero. Thus, by determining the flat band potential one can estimate the situations of conduction and valence band edges for n-type and p-type semiconductors, respectively.⁶ Mott–Schottky theory describes the properties of semiconductor electrolyte interface using space charge capacitance as follows⁷⁷–⁷⁹

\[
\frac{1}{C_{SC}^2} = \frac{2}{qN_\epsilon_0} \left( U_{FB} - U_{app} - \frac{kT}{e} \right) 
\]

(2)

where \( \epsilon \) is the relative permittivity of the semiconductor, \( \epsilon_0 \) is the vacuum permittivity and is equal to \( 8.85 \times 10^{-12} \) F m⁻¹; \( q \) is the elementary charge (−1.6 × 10⁻¹⁹ for holes), \( N \) is the carrier charge concentration, \( U_{app} \) is the applied potential, \( U_{FB} \) is the flat band potential, \( T \) is the absolute temperature and \( k \) is the Boltzmann’s constant and is equal to \( 1.381 \times 10^{-23} \) J K⁻¹. The latest term in eqn (2), \( kT/e \), is 0.026 V at 300 K, is small and can be omitted. CSC can be calculated from impedance as, \( C_{SC} = (−1)/(2\pi fZ_i) \) where \( f \) is the frequency and \( Z_i \) is the imaginary part of the impedance. Fig. 5a and b shows Mott–Schottky plots for both samples at a frequency of 10 000 Hz in 0.1 M NaOH in the dark and under illumination.

A fairly large frequency of 10 000 Hz is chosen since fast processes such as charging of double layer and space charge layer capacitors respond at this frequency. Obviously, selecting and recognizing the linear region are difficult. Therefore, since at this frequency, the samples exhibit capacitive behavior and the capacity of the space charge layer is independent of potential, the Nyquist diagrams are in a range of potentials selected from the CVs. It is expected that these diagrams will coincide almost exactly with the region where only the space layer charging occurs.

For this purpose, Nyquist diagrams with 0.05 V potential interval and over a frequency range of 0.1 to 100 000 Hz are plotted in the dark and under illumination in 0.1 M NaOH solution (Fig. S3 and S4†). As illustrated in these figures, Nyquist diagrams over the range −0.24 to −0.12 V for CuMoO₄ and the range −0.30 to −0.18 V for Cu₃Mo₂O₉ in the dark are fairly in good agreement. Therefore, these regions were used for the linear fitting of the Mott–Schottky equation, and the results are shown in Fig. S5 and S6.† A correlation coefficient close to 1
implies a good agreement between the experimental results and the results of the Mott–Schottky theory. The value of $U_{\text{FB}}$ can be determined from the intercept of the fitting line with the Mott–Schottky plot. In Fig. S5 and S6,† the slopes of Mott–Schottky plots for both electrodes are positive; this confirms that the electrodes are n-type semiconductors, and consequently, the lower conduction band edge practically merges with the quasi-Fermi level of electrons. The conduction band edge, $E_C$, can be experimentally estimated using flat band potential ($U_{\text{FB}}$).‡ For this propose, the electrochemical potentials should be related to absolute energy, $E_{\text{abs}}$, and the effects of pH should be considered using the following equations at 25 °C:

$$E_{\text{RHE}}(V) = E_{\text{Ag/AgCl}} + 0.199 + 0.0592pH$$  \hspace{1cm} (3)

$$E_{\text{abs}}(eV) = -4.5 - E_{\text{RHE}}$$  \hspace{1cm} (4)

where $E_{\text{RHE}}$ and $E_{\text{Ag/AgCl}}$ are potentials against the reversible hydrogen electrode and Ag/AgCl reference electrode, respectively.

As can be seen, different values were obtained for the flat band potentials for both samples. The values of $E_C$ for both samples were determined using the $U_{\text{FB}}$ values reported in Table 1 and eqn (3) and (4).

Then, with a method, which has already been described in the electrochemical studies of nanostructured nickel titanate§ and benefits from a combination of optical (DRS) and electrochemical (impedance) spectroscopies, we determined the valence band edges, $E_V$, of both samples with subtracting the values of band gap energies from $E_C$. All band edges for both samples are reported in Table 1 for in the dark and under illumination. According to these data, we outline the experimental electronic band structures of both samples as illustrated in Fig. 6. The $O^{2-}$:2p and $Cu^{2+}$:3d orbitals contribute to the valence band; additionally, $O^{2-}$:2p and $Mo^{6+}$:4d orbitals contribute to the conduction band for both compounds.‡

The density of donor atoms can be calculated using the slope value of Mott–Schottky plots (Fig. S5 and S6†) and eqn (2). The calculated values are shown in Table 1. The density of donor atoms, especially copper atoms, in Cu$_2$Mo$_2$O$_9$ is larger than CuMoO$_4$. Moreover, using $N_D$ values, it is possible to estimate the diffusion length of minor charge carriers (here holes) using the following equations at 25 °C:

$$L = \left(\frac{2\varepsilon\varepsilon_0 kT}{q^2 N_D}\right)^{1/2}$$  \hspace{1cm} (5)

The obtained results are shown in Table 1 considering that the dielectric constants of Cu$_2$Mo$_2$O$_9$ and CuMoO$_4$ are equal to 7.2 (ref. 83) and 7.9,‡ respectively.

One can calculate diffusion length of minority carrier, $L$, and the thickness of the depletion layer, $W_D$, by using $U_{\text{FB}}$, $N_D$ and eqn (2). The values of $N_D$, $L$ and $W_D$ (for $U_{\text{app}} - U_{\text{FB}} = 1$ V) were computed, and the results (accompanied with $U_{\text{FB}}$) are listed in Table 1.

### Table 1

| Sample          | Condition | $U_{\text{FB}}$/V | $N_D$/cm$^{-3}$ | $W_D$/cm | $L$/cm | $E_C$ vs. NHE/V | $E_C$ (abs)/eV | $E_C$ (abs)/eV | $E_B$/eV |
|-----------------|-----------|-------------------|-----------------|----------|---------|-----------------|----------------|----------------|---------|
| CuMoO$_4$       | Dark      | -1.50             | $1.25 \times 10^{21}$ | 8.36 $\times 10^{-8}$ | 9.44 $\times 10^{-9}$ | -0.53           | -4.0            | -6.3            | 2.3     |
|                 | Illumination | -1.29         | $1.38 \times 10^{21}$ | 7.95 $\times 10^{-8}$ | 9.02 $\times 10^{-9}$ | -0.32           | -4.2            | -6.5            | 2.3     |
| Cu$_2$Mo$_2$O$_9$ | Dark      | -1.18             | $1.42 \times 10^{21}$ | 7.48 $\times 10^{-8}$ | 8.49 $\times 10^{-9}$ | -0.21           | -4.3            | -6.4            | 2.1     |
|                 | Illumination | -1.36         | $1.47 \times 10^{21}$ | 7.36 $\times 10^{-8}$ | 8.34 $\times 10^{-9}$ | -0.39           | -4.1            | -6.2            | 2.1     |
This is due to the four-electron-proton transfer mechanism in alkaline media, which is the rate-determining step at high overpotentials. Therefore, to compare CuMoO₄ and Cu₃Mo₂O₉ in electrochemical OERs, one should calculate their potentials and kinetic parameters such as exchange current density and Tafel slope. The overall reaction, which occurs on the surface of the electrocatalyst is:

\[ 4\text{OH}^- + 4h^+ \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \] (7)

During this complex reaction, four electrons are transferred to the valence band of the semiconductor. As shown in Fig. 6, it is expected that the injection of the electrons of \( \text{OH}^- \) to the valence band of Cu₃Mo₂O₉ is more favorable compared to that of CuMoO₄ because of its lower \( E_V \), and consequently, a higher OER activity than CuMoO₄. Fig. 7a shows the comparative LSVs of both samples for OER measured in 0.1 M NaOH solution at 25 °C; they indicate close onset potentials. The dashed line shows the standard potential of OER. As Fig. 7a shows, OER overpotentials of 0.28 and 0.42 V at a current density of 1 mA cm⁻² were obtained for nanostructured Cu₃Mo₂O₉ and CuMoO₄, respectively. These results are in agreement with the diagram of Fig. 6. In addition, these numerical values are in good agreement with the results of Gou et al., who reported an overpotential of 0.325 mV at 50 mA cm⁻² in 1.0 M KOH for Cu₃Mo₂O₉ nanosheet loaded on nickel foam. The obtained Tafel slopes are close to those reported for some nickelates and cobaltates by Bockris and Otagawa, who investigated OER on the surface of different perovskites and developed a common mechanism for OER by emphasizing on electrochemical adsorption of \( \text{OH}^- \) ions followed by desorption of \( \text{OH}^- \) and formation of \( \text{H}_2\text{O}_2 \) as an intermediate that is decomposed into \( \text{O}_2 \). Such a mechanism has also been suggested for RuO₂ (ref. 93) and TiO₂. Scheme 1 was inspired by their work.

Mott–Schottky analysis showed that Cu²⁺ ions are the localized charges in the space charge layer, thus they should be involved in interfacial phenomena. Accordingly, for the adapted mechanism, we supposed that the adsorption of \( \text{OH}^- \) ions occurs on the copper ions. The first step in Scheme 1 is the formation of the adsorbed \( \text{OH}^- \) radicals, which can occur via discharging of both hydroxyl ions and \( \text{H}_2\text{O} \) molecules. However, in alkaline solution, hydroxyl ions reach the surface of electrodes faster than water molecules because of their diffusion coefficient. The second step, which is rds, includes the electrochemical desorption of \( \text{OH}^- \) radicals, the formation of physically adsorbed hydrogen peroxide and \( \text{OH}^- \) vacancy on the surface of these compounds. The next two steps are fast steps and show desorption and decomposition of hydrogen peroxide and the formation of \( \text{O}_2 \) molecules. The final fast step is surface diffusion of \( \text{OH}^- \) into the oxygen vacancy sites. The exchange current densities \( (i_0) \) (measured by extrapolation of the Tafel curves) for 

\[ \begin{align*}
\text{Cu}^{+2} + \text{OH}^- & \Leftrightarrow \text{Cu}^{+2} - \text{OH} + e^- \\
\text{OH}^- & \rightarrow \text{OH} \quad \text{rds}
\end{align*} \]

Scheme 1 OER mechanism by emphasizing on the electrochemical desorption of \( \text{OH}^- \) as the rate-determining step (rds). V denotes an \( \text{OH}^- \) vacancy and dots show physisorbed species.
plot) were calculated, and the values of $6.8 \times 10^{-10}$ and $3.1 \times 10^{-9}$ mA cm$^{-2}$ were obtained for CuMoO$_4$ and Cu$_3$Mo$_2$O$_9$, respectively. Generally, the exchange current density is expected to be proportional to the surface density of catalytically active sites; here, Cu$^{2+}$ ions correspond to the below mechanism.

After investigating the OER activity, the electrocatalytic performances of the samples were comparatively studied in terms of HER in 0.1 M NaOH solution at 25 °C. For this purpose, the LSVs of both samples were taken by starting from positive potentials to negative potentials up to the occurrence of HER, which is identified by a sharp increase in cathodic current. The resulting LSVs are depicted in Fig. 8a. It is observed that some cathodic peaks exist before hydrogen evolution. Liu et al. showed that the redox reaction of Mo in copper molybdate does not occur during electrochemical measurement, so the redox behavior of Mo has no contribution to the measured capacitance. Moreover, our previous study on the comparative electrochemical behaviors of CuWO$_4$ and CuO showed that these peaks can be attributed to Cu(n)/Cu(i) and Cu(i)/Cu(0) redox reactions.$^{64}$ Cyclic voltammograms (Fig. S7) show more detail on these redox reactions for both samples. These cyclic voltammograms clearly show that the reduction of copper ions to copper atoms occurs before HER. Therefore, HER occurs on the surface of molybdate-derived copper atoms. In fact, HER takes place in acidic media more facile than in alkaline solution. However, using acidic electrolyte has some disadvantages, such as the corrosion of the electrolyzer.$^{98}$

Moreover, the reaction needs more energy to produce proton by O–H bond cleavage of water molecules in alkaline solution.$^{29}$ The elementary steps for HER in alkaline solution accompanied by their Tafel slopes are:

**Volmer step** (120 mV dec$^{-1}$):

$$\text{H}_2\text{O} + \text{M} + \text{e} \rightarrow \text{M}^- \cdot \text{H} + \text{OH}^- \quad (8)$$

**Heyrovsky step** (40 mV dec$^{-1}$):

$$\text{H}_2\text{O} + \text{M}^- \cdot \text{H} + \text{e} \rightarrow \text{M} + \text{H}_2 + \text{OH}^- \quad (9)$$

**Tafel step** (30 mV dec$^{-1}$):

$$\text{M}^- \cdot \text{H} + \text{M}^- \cdot \text{H} \rightarrow 2\text{M} + \text{H}_2 \quad (10)$$

Based on these steps, two mechanisms of Volmer–Heyrovsky and Volmer–Tafel are possible. The Volmer step, which is the water dissociation step, is common in both mechanisms. The energy required for this step can be provided by the adsorption of water molecules on the surface of the electrocatalyst.$^{100}$ The stronger the water molecules adsorption the more the energy provided for the Volmer step. In addition, adsorption of OH$^-$ ions on the active sites has a poisoning effect and increases the overpotential by lowering the activity because of limiting the number of sites in alkaline solution. The hydrogen binding energy is another important factor that governs the HER activity of the catalysts. In fact, a volcano-type correlation between HER exchange current densities and H-binding energy values was demonstrated, which was supported by both DFT and experimental studies.$^{101,102}$ Furthermore, the crystallographic planes...
of the catalysts\textsuperscript{48,49} and the existence of an active component for water dissociation\textsuperscript{44} can affect the kinetics of the reaction.

As illustrated in Fig. 8a, the HER overpotential on the surface of Cu$_3$Mo$_2$O$_9$ has a value of around 0.1 V, which is smaller than that of CuMoO$_4$ at a current density of 0.4 mA cm$^{-2}$. Because the adsorbed molecules (here, water) and the active sites (here, copper atoms) are the same in nature, the predominant factor should be the number of active sites. It is clear that the surface density of copper atoms on the surface of Cu$_3$Mo$_2$O$_9$ is larger than that of CuMoO$_4$, so more surface sites are available for HER on the surface of Cu$_3$Mo$_2$O$_9$; this lowers the overpotential. Moreover, although a precise look indicates copper active sites, copper atoms have different arrangements and different sub-layers. Reduction of copper ions to copper occurs on the surface layer of copper molybdates, and the oxygen species, which exist in the sublayers, facilitate water molecules adsorption, causing HER promotion.\textsuperscript{105,106} Our previous work on the comparative studies of CuWO$_4$ and CuO showed that the sublayer atoms have a considerable effect on lowering HER overpotentials.\textsuperscript{48} The effects of the nature of sublayer atoms and their configurations on reducing the HER overpotential on the surface of copper were already reported by Zhang et al.; they investigated full water splitting on sulfur-doped copper oxide in comparison with metallic copper.\textsuperscript{107}

Fig. 8b shows a Tafel slope close to 120 mV dec$^{-1}$ for both samples highlighting that the Volmer step is the rate-determining step in HER mechanism for both samples. The Tafel slopes of 166 and 152 mV dec$^{-1}$ were obtained, and accordingly, exchange current densities of $1.5 \times 10^{-6}$ and $4.5 \times 10^{-6}$ A cm$^{-2}$ were calculated for CuMoO$_4$ and Cu$_3$Mo$_2$O$_9$, respectively. It means that the rate of HER on the surface of Cu$_3$Mo$_2$O$_9$ is three times faster compared to CuMoO$_4$, which can be expected because of the more accessible active sites of this compound. The number of surface sites was also used for identifying the smaller Tafel slope for HER on the surface of MoS$_2$.\textsuperscript{108,109} Additionally, these results are in agreement with our previous findings that compared CuWO$_4$ and CuO.\textsuperscript{44} We showed that exchange current density for HER on the surface of CuO is much larger than that of CuWO$_4$. Similarly, as shown in Fig. 1, the structural difference between CuMoO$_4$ and Cu$_3$Mo$_2$O$_9$ is that the latter has one CuO unit for each CuMoO$_4$ pair, i.e., Cu$_3$Mo$_2$O$_9 \equiv 2$CuMoO$_4$ + CuO, and because of the existing CuO unit, Cu$_3$Mo$_2$O$_9$ has a larger exchange current density. At the final step of our electrochemical studies, we investigated the ability of both samples for CO$_2$ reduction. Therefore, we purged the 0.1 M NaOH solution with CO$_2$ for at least 30 min. The pH of the solution decreased from 13 to around 7 because of the following equilibrium:

\[
\text{OH}^- (\text{aq}) + \text{CO}_2(\text{aq}) \rightleftharpoons \text{HCO}_3^- (\text{aq}) \quad (11)
\]

\[
\text{OH}^- (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightleftharpoons \text{CO}_3^{2-} (\text{aq}) \quad (12)
\]

At ambient temperature and natural pH, the major species inside the solution is HCO$_3^-$\textsuperscript{110} Fig. 8c and d illustrate that HER takes place in more negative potentials when CO$_2$ is bubbled into the solution, and consequently, CO$_2$ and its related species HCO$_3^-$ and CO$_3^{2-}$ are present in the solution, i.e., the HER overpotential increases for both samples.

For investigating this process in more detail, we compared the cyclic voltammograms of both compounds with and without CO$_2$ bubbling. The results are presented in Fig. S8.\textsuperscript{†}

Both cathodic and anodic peaks of the samples in CO$_2$ saturated 0.1 M NaOH solution show a significant decrease in height. This indicates that the adsorption of CO$_2$ and maybe its reduction intermediates occur on the same sites where HER occurs. Furthermore, the adsorption of CO$_2$ has a poisoning effect on HER and inhibits it.

In fact, there is a competition between H$_2$O and CO$_2$ molecules to be reduced on the surface of copper atoms.\textsuperscript{111,112} However, according to Fig. 8c and d, when CO$_2$ is blown into the NaOH solution, the increasing of HER overpotential for CuMoO$_4$ is more than that of Cu$_3$Mo$_2$O$_9$ by around 0.15 V.

It means that the dissolved CO$_2$ species in the solution or the adsorbed CO$_2$ reduction intermediates occupy more HER active sites on the surface of CuMoO$_4$ compared to Cu$_3$Mo$_2$O$_9$. This implies the fact that the density of active sites (here, copper atoms) on the surface of Cu$_3$Mo$_2$O$_9$ is higher compared to CuMoO$_4$. Moreover, the atoms and their configuration in the sublayer have a considerable effect on the adsorption of CO$_2$.

The Tafel slope analysis for HER in the presence of CO$_2$ shows the same value of exchange current density of $1.5 \times 10^{-6}$ A cm$^{-2}$, for both samples, whereas Cu$_3$Mo$_2$O$_9$ has a larger surface density of active sites for HER. Actually, it is possible that when HER starts on Cu$_3$Mo$_2$O$_9$, some sites have still been occupied by CO$_2$ reduction species. According to our previous report,\textsuperscript{44} which showed that, in the presence of CO$_2$-species in the solution, HER occurs more readily than CuWO$_4$. Therefore, it is possible here that HER occurs on the surface of copper atoms, which have come from CuO unit of Cu$_3$Mo$_2$O$_9$, while CO$_2$-species involved in the reaction on the surface of copper atoms have originated from CuMoO$_4$ units of Cu$_3$Mo$_2$O$_9$. This means that the adsorption of CO$_2$-species is strong on the surface of CuMoO$_4$.

In fact, the existence of oxygen in sublayers causes the strong adsorption of CO$_2$, which will produce carbon-rich CO$_2$-reduction products such as alcohols, carboxylic acids and hydrocarbons instead of CO. This conclusion can be supported by other reports. For instance, it has been reported that oxide-derived copper produces methanol,\textsuperscript{113,114} ethylene and ethanol with increased current efficiency.\textsuperscript{116} Moreover, the existence of tin oxide layer over tin effectively produces formate\textsuperscript{117,118} and formic acid.\textsuperscript{119} Tayebi et al. used DFT calculation for electrochemical reduction of CO$_2$ for producing methanol, methane and formic acid over different transition metal oxides, and showed that there is a volcano-shaped behavior through the scaling relations of adsorbed intermediates.\textsuperscript{120}

4. Conclusion

In this study, two types of copper molybdate, CuMoO$_4$ and Cu$_3$Mo$_2$O$_9$, were synthesized successfully in nanoscale. Our results showed that the difference between their electrochemical behaviors strongly depends on their crystal structure.
In fact, the existence and addition of CuO unit in the unit cell of Cu$_3$Mo$_2$O$_9$ caused a modified behavior corresponding to a combination of CuO and CuMoO$_4$.

The value of the Tafel slope for Cu$_3$Mo$_2$O$_9$ (as OER) was much lower than that for CuMoO$_4$. Therefore, Cu$_3$Mo$_2$O$_9$ shows a better catalytic performance for both HER and OER in 0.1 M alkaline solution. The literature review indicated that Cu$_3$Mo$_2$O$_9$ could be a bifunctional water splitting catalyst under alkaline conditions, and show better activity at low cell voltage than CuMoO$_4$. The superior OER and HER activities for Cu$_3$Mo$_2$O$_9$ can be attributed to the more active sites arising from oxygen vacancies or the unique topology of Cu$_3$Mo$_2$O$_9$ crystals that maximizes the number of exposed active sites. However, our investigation showed that CO$_2$-species are adsorbed on the surface of CuMoO$_4$ more strongly than on the surface of Cu$_3$Mo$_2$O$_9$, so they may produce more stable and carbon-rich products.

**Conflicts of interest**

There are no conflicts to declare.

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