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# Spinel cobalt-based binary metal oxides as emerging materials for energy harvesting devices: synthesis, characterization and synchrotron radiation-enabled investigation†

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The synthesis and characterization of spinel cobalt-based metal oxides ( $\text{MCo}_2\text{O}_4$ ) with varying 3d-transition metal ions (Ni, Fe, Cu, and Zn) were explored using a hydrothermal process (140 °C for two hours) to be used as alternative counter electrodes for Pt-free dye-sensitized solar cells (DSSCs). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed distinct morphologies for each metal oxide, such as  $\text{NiCo}_2\text{O}_4$  nanosheets,  $\text{CuCo}_2\text{O}_4$  nanoleaves,  $\text{FeCo}_2\text{O}_4$  diamond-like, and  $\text{ZnCo}_2\text{O}_4$  hexagonal-like structures. The X-ray diffraction analysis confirmed the cubic spinel structure for the prepared  $\text{MCo}_2\text{O}_4$  films. The functional groups of  $\text{MCo}_2\text{O}_4$  materials were recognized in metal oxides throughout Fourier transform infrared (FTIR) analysis. The local structure analysis using X-ray absorption fine structure (XAFS) at Fe and Co K-edge identified octahedral (Oh)  $\text{Co}^{3+}$  and tetrahedral (Td)  $\text{Co}^{2+}$  coordination, with  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  favoring Td sites, while  $\text{Ni}^{3+}$  and  $\text{Fe}^{3+}$  preferred Oh active sites. Further investigations utilizing the Fourier transformation (FT) analysis showed comparable coordination numbers and interatomic distances ranked as  $\text{Co-Cu} > \text{Co-Fe} > \text{Zn-Co} > \text{Co-Ni}$ . Furthermore, the utilization of  $\text{MCo}_2\text{O}_4$  thin films as counter electrodes in DSSC fabrication showed promising results. Notably, solar cells based on  $\text{CuCo}_2\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$  counter electrodes showed 1.9% and 1.13% power conversion efficiency, respectively. These findings indicate the potential of employing these binary metal oxides for efficient and cost-effective photovoltaic device production.

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## Introduction

Because of the permanent growth in the global population and industrialization, the demand for energy has increased steadily. Limits in fuel-based energy sources make the need for cleaner, sustainable alternative energy sources inevitable. Among all renewable energy sources, solar energy is one of the most impressive ones. Photovoltaic technologies, particularly dye-sensitized solar cells (DSSCs), have emerged as key factors in

this transition owing to their low cost and easy production processes. Another important parameter that increases the impression of DSSCs is the capability of harvesting energy from even lower-intensive light.

Significant effort has been devoted to increasing the power conversion efficiency and stability of DSSCs while making them cost-effective. To achieve optimal performance in the DSSCs, the counter electrode commonly incorporates platinum (Pt) on a surface of transparent conductive oxide.<sup>1,2</sup> Several novel approaches have been formulated to improve the DSSCs' performance including enhancing the light absorption capacity of the sensitizer, charge separation of photo-induced charge at the electrolyte-semiconductor interface, and prompt the migration of charge towards the counter electrode.<sup>3-5</sup> The proposed approaches involve the binding of a sensitizer onto wide bandgap semiconductor substrates such as titanium dioxide, which aims to enhance light absorption capabilities.<sup>6</sup> Additional efforts have been made to replace the Pt counter electrode in DSSCs. As an alternative to Pt, various kinds of materials, including metal oxides, metal sulfides, carbon, and hybrid electrodes, have been proposed to obtain cost-effective

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device fabrication.<sup>7–11</sup> An alternative candidate with significant potential for DSSCs is spinel cobalt-based metal oxides ( $\text{MB}_2\text{O}_4$ , M: tetrahedral, B: octahedral sites). Such unique characteristics involve excellent electrical conductivity, efficient charge transfer, and significantly large surface area. Besides that, various oxidation states, and notable electrochemical activity make them highly advantageous to be used in energy and photocatalytic applications.<sup>12–15</sup>

The spinel cobalt oxide ( $\text{Co}_3\text{O}_4$ ) is one of the most investigated electro-catalyst materials that is widely applied in the counter electrode for DSSCs. The tetrahedral site (Td) is occupied by  $\text{Co}^{2+}$  ions, while the octahedral site (Oh) is occupied by two  $\text{Co}^{3+}$  ions.<sup>16</sup> To date,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  serve as active sites within the spinel cobalt metal oxide  $\text{Co}_3\text{O}_4$ , and they have been reported to have a crucial role in charge transfer and their catalytic activity.<sup>17–19</sup> Recent studies report that replacing the 3rd transition metal ions, such as Ni and Zn ions, with the  $\text{Co}^{2+}$  in spinel cobalt oxide ( $\text{Co}_3\text{O}_4$ ) enhances their electrical conductivity.<sup>20</sup> For instance,  $\text{ZnCo}_2\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  exhibited superior electrical conductivity compared to  $\text{Co}_3\text{O}_4$ .  $\text{Zn}^{2+}$  ions are beneficial for indicating defects in the Td sites,<sup>17–20</sup> as observed in spinel oxides, which in turn enhances the catalytic activity for the oxygen evolution reaction. Moreover, the large surface and electrical conductivity of  $\text{NiCo}_2\text{O}_4$  result in better catalytic activity than spinel metal oxide ( $\text{Co}_3\text{O}_4$ ). Also, the  $\text{Fe}^{3+}$  in  $\text{FeCo}_2\text{O}_4$  occupies the Oh sites, leading to a shift in energy level near the Fermi level, which improves the activity of spinel metal oxide.<sup>21,22</sup>

Several reports have integrated the spinel-based cobalt structure into DSSC devices. Interestingly, the  $\text{Co}_3\text{O}_4$  counter electrode of PCE  $\sim 8.6\%$  in DSSCs exhibits an excellent catalytic performance towards the iodide electrolyte compared to the Pt standard counter electrode.<sup>23</sup> It has been reported also that,  $\text{Co}_3\text{O}_4$  has a good electro-catalytic activity towards reduction of  $\text{I}_3^-$  ions into  $\text{I}^-$  ions.<sup>24</sup> Furthermore, zinc substitution for Co in cobalt oxide(II,III) results in the spinel structure of Zn–Co–O with p-type conductivity. The hole transport layer of Zn–Co–O

employed in DSSCs results in enhanced diffusion length and transport within a device.<sup>25</sup> The DSSCs based spinel  $\text{NiCo}_2\text{O}_4$  nanostructures reported high performance and are comparable to the Pt counter electrode.<sup>26</sup> To address, the role of the local structure of the spinel-based cobalt materials in DSSCs performance still needs in-depth investigation.

In the present work, three-dimensionally arrays of spinel cobalt-based metal oxide thin films of  $\text{MCo}_2\text{O}_4$  (M: Ni, Fe, Cu, Zn) were fabricated through hydrothermal deposition to use them as counter electrodes to obtain cost-effective DSSCs. Surface morphology and roughness of the prepared samples were investigated throughout SEM and AFM analysis. The XAFS technique is employed to examine the atomic coordination and interatomic distances by observing the local structure at Fe and Co K-edge. Also, the XANES spectra indicate the prepared samples have a spinel structure. Then, spinel cobalt-based metal oxide thin films were used in the fabrication of DSSCs as promising counter electrodes, and the photovoltaic performance of DSSCs with  $\text{MCo}_2\text{O}_4$  counter electrodes were compared.

## Experimental procedures

The following materials are used to synthesis the spinel cobalt based oxide films: copper nitrate tetrahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), iron monohydrate ( $\text{Fe}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ), nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), hexamethylenetetramine (HMTA,  $(\text{CH}_2)_6\text{N}_4$ ), and indium tin oxide (ITO) coated glasses, all are purchased from Sigma Aldrich and used without any further purification.

The samples were grown hydrothermally using a solution processing route. The synthesis of spinel cobalt-based metal oxide thin films,  $\text{MCo}_2\text{O}_4$ , coated over a cleaned ITO substrate is shown in Fig. 1. The ITO substrate was subjected to cleaning in the acetone for 15 min followed by 15 min in the ethanol under sonication. The preparation procedure was performed by

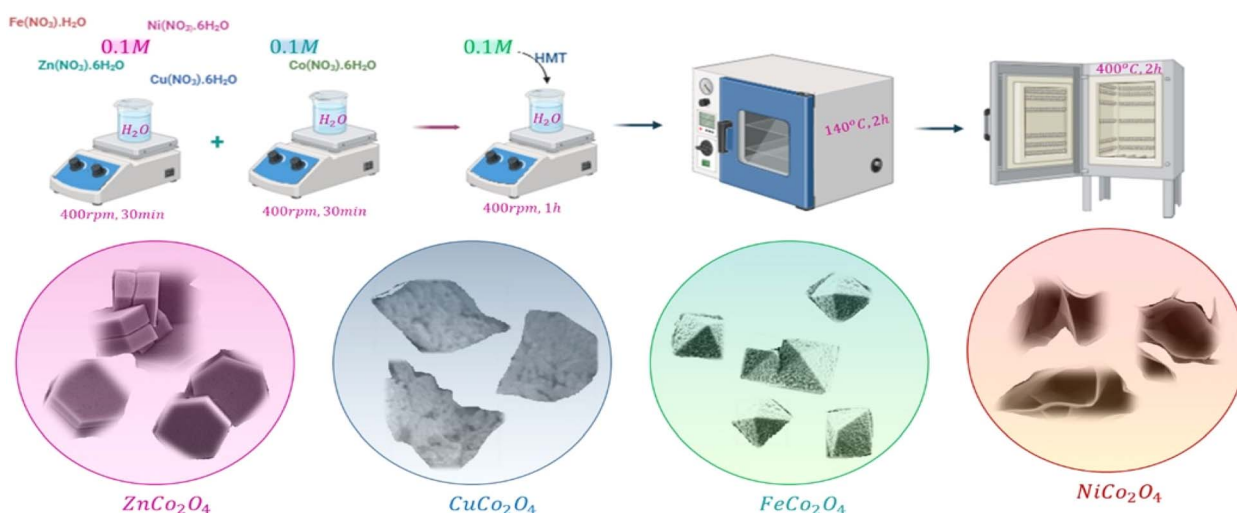


Fig. 1 A schematic illustration depicting the deposition procedures of spinel cobalt-based samples.



mixing 0.1 M of  $M(NO_3)_2 \cdot xH_2O$  dissolved in 40 mL deionized water, and 0.1 M of  $Co(NO_3)_2 \cdot 6H_2O$  dissolved in 40 mL deionized (DI) water. The solution was then stirred at 400 rpm for 30 min. Then, the 0.1 M of  $(CH_2)_6N_4$  was added to the prepared aqueous solution. The obtained stock solutions were then transferred into a glass-sealed bottle containing a cleaned ITO substrate before being grown in an oven at 140 °C for two hours. Finally, the deposited spinel cobalt-based metal oxides of  $MCo_2O_4$  films were rinsed with deionized water and annealed at 400 °C in a furnace for another two hours.

Scanning electron microscopy (SEM, Quanta FEG 450) was conducted to investigate the morphology and size distribution of the metal oxide samples. The surface roughness of the  $MCo_2O_4$  thin films was carried out by using an atomic force microscope (AFM, SmartSPM™ 1000), FTIR (Bruker Vertex 80 and Hyperion 2000 microscope) used to investigate the vibrational modes and chemical bonds of metal oxides. The XAFS data were obtained *via* the BM-08 XAFS/XRF beamline at the Synchrotron-Light for Experimental Science and Applications in the Middle East (SESAME). The beamline was run in decay condition at an energy level of 2.5 GeV, with 300 mA as a maximum current. The X-ray absorption fine structure (XAFS) data were measured on the BM08-XAFS/XRF beamline of the SESAME operated at 2.5 GeV in “decay” mode with a maximum electron current of 300 mA.<sup>27</sup> The XAFS spectra of the materials were acquired in transmission mode in the spectral range of Co K-edge (7709 eV) and Fe K-edge (7112 eV) at room temperature. The X-ray beam intensity was measured by ionization chambers filled with an optimal mixture of noble gases at a total pressure of 1.0 bar, and the XAFS data of the samples were acquired from the signals measured at ion chambers subsequently amplified by Stanford picoammeters and digitalized by a voltage to frequency converter, using a double-crystal Si (111) monochromator. The energy was calibrated at the Co K-edge (7709 eV)

and Fe K-edge (7112 eV) of the Co and Fe standard metal foils, respectively. The sample was prepared in pallet form (13 mm diameter) by pressing a homogeneous mixture of calculated quantity of finely ground material and polyvinylpyrrolidone (PVP) powder. The amount of material in the pellet was calculated using XAFS mass software to give an absorption  $\mu t \sim 1.5$ , just above the Co K-edge and Fe-K edge absorptions.

The DSSCs were prepared using  $TiO_2$  nanoparticle decorated ITO coated photoanodes. The electrodes were sintered at 450 °C in air ambient for 30 min to remove contaminations from the  $TiO_2$  nanoparticle surfaces. And then was immersed in N719 dye for a night. The photoanodes were washed with ethanol and dried using a heat gun.  $MCo_2O_4$  coated ITO counter electrodes and dye-coated  $TiO_2$  photoanodes were sealed together and an electrolyte (iodide/tri-iodide in a nitrile solvent) was used to fill the space between two electrodes. The performances of DSSCs were measured under a class A solar simulator (ABET Technology Sun2000) with an AM 1.5 G filter and  $100 \text{ mW cm}^{-2}$  light intensity using a Keithley 2425 source meter.

## Results and discussion

The DSSCs device performance is directly influenced by the morphology of the counter electrode in particular redox/oxidation electrolyte at the interface. SEM images can give insight into crystal arrays and defective surfaces of spinel cobalt oxides. The surface morphologies of as-prepared  $MCo_2O_4$  thin films are illustrated in Fig. 2. Interestingly, the morphology of the prepared samples can be correlated to the variations in source metal ions. Fig. 2(a) and (b) manifested uniform arrays of nano-leave structures that coincide with the  $CuCo_2O_4$  thin film. Whereas Fig. 2(c) and (d) displays uniform arrays of octahedral-shaped structures observed in the  $FeCo_2O_4$  thin film. The  $FeCo_2O_4$  thin film is comprised of nano-blocks with average size of about 500 nm. The observed octahedron structure

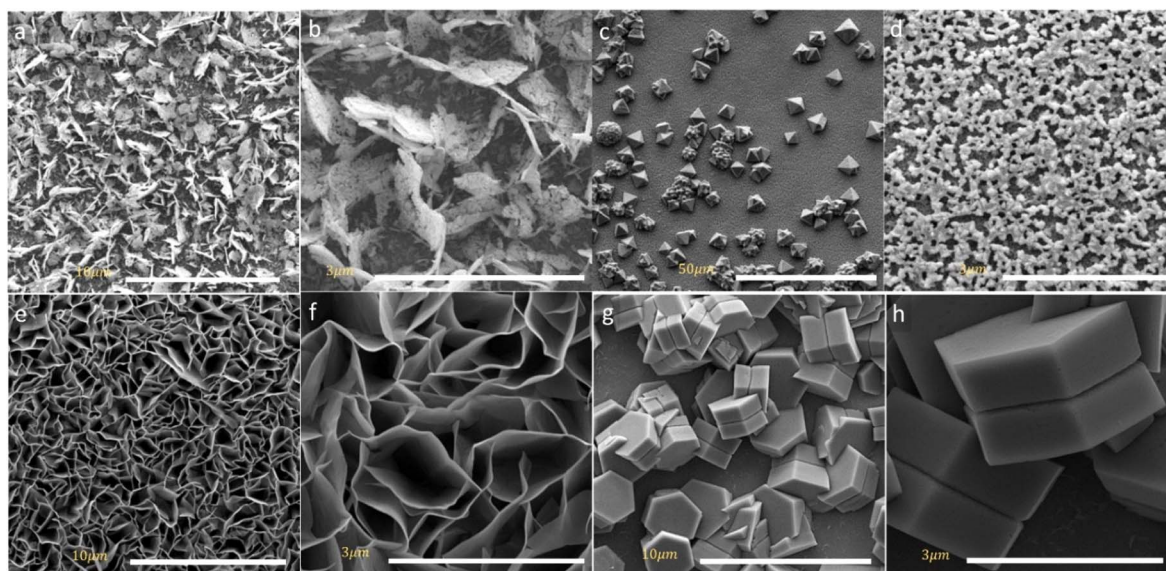


Fig. 2 SEM images of the obtained (a and b)  $CuCo_2O_4$  thin film (c and d)  $FeCo_2O_4$  thin film (e and f)  $NiCo_2O_4$  thin film and (g and h)  $ZnCo_2O_4$  thin film.





demonstrates high-pressure conditions controlled by the (111) plane, devoid of any preferential axis for selective growth.<sup>28</sup> Fig. 2(e) and (f) displays a hierarchical structure of  $\text{NiCo}_2\text{O}_4$  nano-sheets observed with hollow arrays. Fig. 2(g) and (h) depicts a twin hexagonal configuration of nano-block  $\text{ZnCo}_2\text{O}_4$  arrays observed with non-uniform distribution due to anisotropic growth along [100] and [001] directions.<sup>29</sup> It is impressive to find that different  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  reacted species tend to form spinel structures in a cubic crystal phase. The intricate reaction pathways of these species during the hydrothermal process drive the formation of distinct morphologies of spinel metal oxides. Initially, the decomposed reacted species undergo a recrystallization process to form  $\text{MCo}_2\text{O}_4$  with preferential growth on selective planes, depending on the nature of the ions. The synthesis of  $\text{MCo}_2\text{O}_4$  is driven by the formation of  $\text{M}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  before transforming into  $\text{MCo}_2(\text{OH})_6$  complex compound, as demonstrated by the NR Chodankar group.<sup>30</sup> Alternatively, another reaction route suggests that the formation pathway is governed by the formation of  $\text{Co}_3\text{O}_4$  and  $\text{MO}$ , which are then reduced to the  $\text{MCo}_2\text{O}_4$  structure.<sup>31</sup> The annealing process reduces the  $\text{OH}^-$  ions in the complex compound to the oxide form, resulting in the obtaining of bimetal oxides.

The HMT acts as an alkaline source that assists in the formation of M-Co precursor. During the hydrolysis of HMT,  $\text{NH}_3$  is released, making the solution alkaline. This process also produces  $\text{OH}^-$  ions in the hydrothermal synthesis, which react with  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$  ions to form spinel metal oxide. Furthermore, studies have found HMT useful for obtaining a crystalline spinel metal oxide structure. The alkaline environment facilitated by HMT is preferable for precipitating  $\text{M}^{2+}$  and  $\text{Co}^{2+}$  ions during hydrothermal deposition, accelerating the formation of the crystalline  $\text{MCo}_2\text{O}_4$  structure.<sup>32,33</sup>

The surface area and roughness of the electrodes can provide significant insight into understanding the charge transfer

mechanism and overall device performance. The AFM imaging was performed for the  $\text{MCo}_2\text{O}_4$  thin films and illustrated in Fig. 3. The AFM images of the prepared  $\text{CuCo}_2\text{O}_4$  thin film exhibit a high root mean square (RMS) roughness of  $0.16 \mu\text{m}$  and a large surface area of  $38.74 \mu\text{m}^2$ . While the  $\text{FeCo}_2\text{O}_4$  thin films show a polygon-shaped structure with an overall RMS of  $0.03 \mu\text{m}$  and a surface area of  $29.9 \mu\text{m}^2$ . The phase image demonstrates a variation between  $-50^\circ$  and  $20^\circ$  indicating low phase separation at the grain boundaries. The  $\text{NiCo}_2\text{O}_4$  nano-sheets thin films depict a large surface area of  $58.87 \mu\text{m}^2$  and RMS of  $0.26 \mu\text{m}$  with an average thickness of nearly  $20 \text{ nm}$ , while a high roughness was observed for the hexagonal structure of  $\text{ZnCo}_2\text{O}_4$  with an RMS of  $0.35 \mu\text{m}$  and surface area of  $34.9 \mu\text{m}^2$ . The hexagonal plates of  $\text{ZnCo}_2\text{O}_4$  are stacked in a non-uniform structural array.

In DSSCs, the device performance is highly dependent on the crystal quality of the counter electrode based a binary metal oxide films. The cubic spinel structure was confirmed for various metal oxide films from crystallographic X-ray diffraction plots in Fig. S1.† As seen, the diffracted XRD peaks of  $\text{FeCo}_2\text{O}_4$  film match the (220), (311), (400), (422), and (440) crystal planes indexed to  $Fd3m$  space group (JCPDS card No. 04-0850). The crystal profile of  $\text{NiCo}_2\text{O}_4$  nano-sheets assigned to (111), (220), (311), (222), (400), (331), and (511) crystal planes suggested  $Fd3m$  space group (JCPDS card No. 01-073-1702). For  $\text{CuCo}_2\text{O}_4$  nano-leaves, the observed XRD profile in agreement with (111), (220), (311), (400), (422), and (511) crystallographic planes analogue to  $Fd3m$  space group (JCPDS card No. 23-1390). The  $\text{ZnCo}_2\text{O}_4$  tends to form a crystal structure throughout hydrothermal synthesis similar to the above metal oxide films. The crystal diffraction profile of  $\text{ZnCo}_2\text{O}_4$  resembles (220), (311), (222), (511), and (620) crystal planes for  $Fd3m$  (227) space group (JCDP card No. 00-001-1149).

The UV-vis-NIR spectral of the spinel metal oxide films plots in Fig. S2† and the corresponding extrapolated absorption band gap energies ( $E_g$ ) were determined according to Tauc plot. The  $\text{NiCo}_2\text{O}_4$  nanosheets exhibit higher absorbance compared to the other spinel materials oxides followed by crystal  $\text{CuCo}_2\text{O}_4$  nanoleaves. The straight-line interception yields two band gap energies of 1.98 and 2.50 eV for  $\text{ZnCo}_2\text{O}_4$ , while the obtained band gap energies of 2.00 and 3.35 eV for  $\text{NiCo}_2\text{O}_4$  in agreement with the reported values of 2.00 and 3.30 eV.<sup>34</sup> The valence band in  $\text{NiCo}_2\text{O}_4$  was constructed from O 2p orbital and the conduction band from 3d orbitals of Ni and Co. And has an electron configuration of tetrahedral high spin  $\text{Co}^{2+}$  ( $\text{eg}^4 \text{t}_{2g}^3$ ), octahedral low spin  $\text{Co}^{3+}$  ( $\text{t}_{2g}^6$ ), and  $\text{Ni}^{3+}$  ( $\text{t}_{2g}^6 \text{eg}^1$ ). Therefore, the electron can be excited from Co-3d- $\text{t}_{2g}$  to the partially filled Co 3d-eg orbital. Consequently, the presence of two band gap energies can be assigned to high spin and low spin of  $\text{Co}^{3+}$  in the spinel structure.<sup>34</sup> The spinel  $\text{CuCo}_2\text{O}_4$  band gap energies was 1.88 eV and 3.0 eV and  $\text{FeCo}_2\text{O}_4$  yields 2.18 eV and 2.82 eV. The determined values are close to those reported in the literature.<sup>35,36</sup>

The solution processed DSSCs device *via* hydrothermal usually contains -OH functional group. To verify the presence of the -OH group and other functional groups that could influence the device performance, the FTIR profile illustrated in Fig. 4

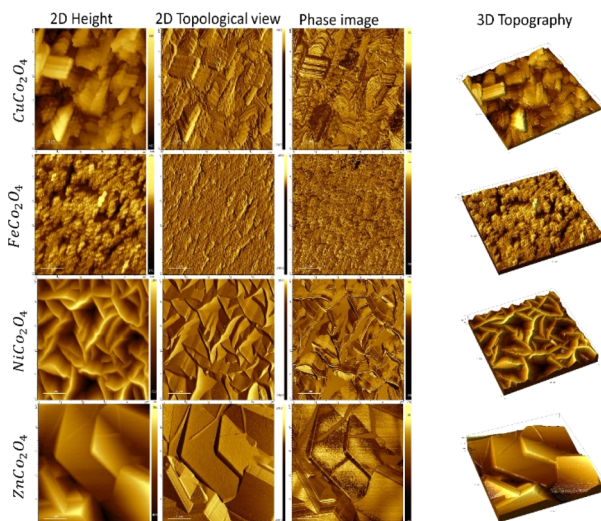


Fig. 3 AFM images of as-deposited metal oxides of  $\text{NiCo}_2\text{O}_4$ ,  $\text{CuCo}_2\text{O}_4$ ,  $\text{ZnCo}_2\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4$ , and  $\text{FeCo}_2\text{O}_4$  in 2D and 3D profile.



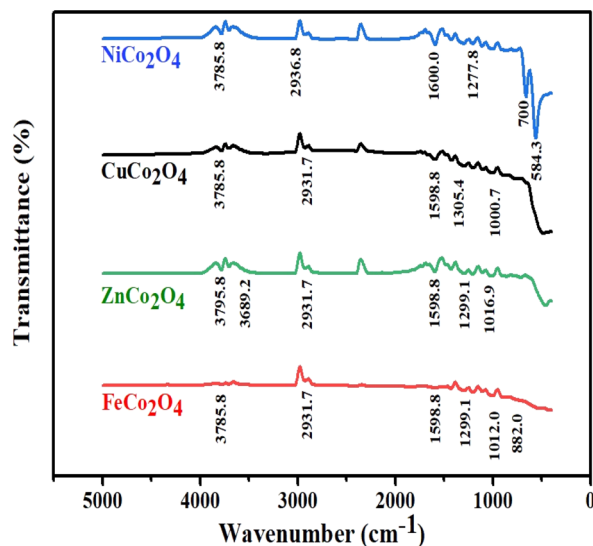


Fig. 4 FTIR profile of the prepared binary metal oxide films  $\text{MCo}_2\text{O}_4$ .

corresponds to the prepared  $\text{MCo}_2\text{O}_4$  films. The vibration modes that match the M–O group can be seen at  $584.3\text{ cm}^{-1}$  in various sample profiles. The M–O vibration modes at  $584.3\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$  may be associated with octahedral and tetrahedral sites.<sup>37</sup> Furthermore, stretching modes located at approximately  $882\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  are assigned to the C–O group. Furthermore, the weak vibrational mode at  $1277.8\text{ cm}^{-1}$  and  $1299.1\text{ cm}^{-1}$  is linked to the  $\text{NO}_3^-$  group.<sup>38</sup> Additional stretching characteristics identified at  $1598.8\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  were assigned to COO and C=O molecules.<sup>39</sup> The stretching modes at  $2931.7\text{ cm}^{-1}$ ,  $2936.8\text{ cm}^{-1}$ ,  $3785.8\text{ cm}^{-1}$ , and  $3795.8\text{ cm}^{-1}$  are attributed to the O–H functional group.<sup>40,41</sup> A higher content of OH- molecules was noticed in the case of  $\text{ZnCo}_2\text{O}_4$  associated with a prominent shift in the OH vibration mode.

The local structure of the  $\text{MCo}_2\text{O}_4$  thin films could play an effective role in the DSSC device performance. The applied XAFS integrates to resolve the local structure of spinel cobalt oxide devices. The XANES spectra at Co absorption K-edge are presented in Fig. 5 of the prepared samples. Resolving the  $\text{FeCo}_2\text{O}_4$  structure at the Co absorption K-edge is elusive and therefore XANES is applied at the Fe absorption K-edge. According to the XANES data, the Co absorption K-edge was  $(7722.53\text{ eV})$  for  $\text{NiCo}_2\text{O}_4$ ,  $(7724.02\text{ eV})$  for  $\text{CuCo}_2\text{O}_4$  and  $(7722.18\text{ eV})$  for  $\text{ZnCo}_2\text{O}_4$ . The observed Co absorption K-edge aligns with the value reported in the literature at  $7721.4\text{ eV}$ , while the Fe absorption K-edge was  $7125.53\text{ eV}$  for  $\text{FeCo}_2\text{O}_4$ . The oxidation state of the cobalt cation is  $\text{Co}^{3+}$  and the observed XANES spectrum reveals the spinel structure of the prepared samples.<sup>42,43</sup>

The observed XANES spectrum reveals a low-intensity pre-edge peak at A, which can be assigned to  $1s \rightarrow 3d$  quadrupole transition in spinel cobalt oxide ( $\text{Co}_3\text{O}_4$ ).<sup>44</sup> A transition edge (shoulder region) was observed at B, along with the prominent white-line peak of high intensity at C. These transition edges at

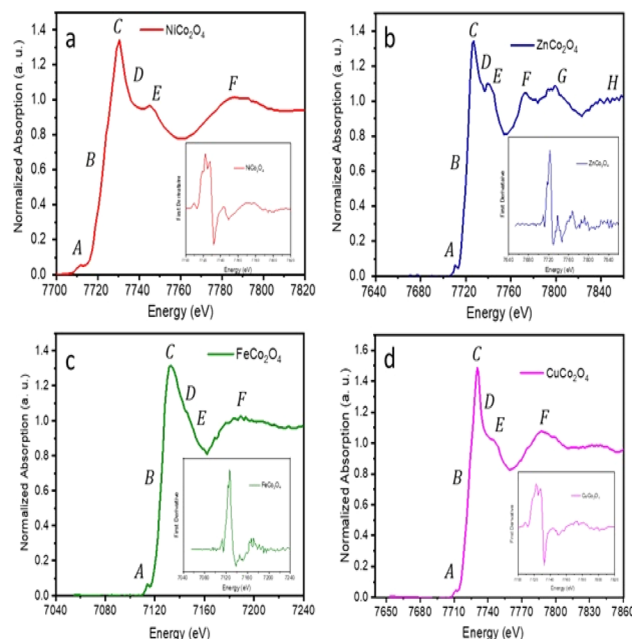


Fig. 5 XANES spectra collected at Fe and Co K-edge of (a)  $\text{NiCo}_2\text{O}_4$ , (b)  $\text{ZnCo}_2\text{O}_4$ , and (c)  $\text{CuCo}_2\text{O}_4$  collected at Co K-edge and (d)  $\text{FeCo}_2\text{O}_4$  collected at Fe K-edge; inset figures illustrate the corresponding first derivative of the absorption spectra.

B and C can be attributed to resonance peaks.<sup>45,46</sup> The white-line region can be ascribed to the  $1s \rightarrow np$  transition.<sup>46</sup>

Following that, minor peaks of low intensity were observed at D and E. The broadening of peak D, in particular, in  $\text{FeCo}_2\text{O}_4$  can be attributed to the coordination atoms in the vicinity of the Co absorber atom. Moreover, two peaks at E and F indicate the presence of multiple scattering associated with the coordination of the medium-range structure surrounding the Co absorber atom.<sup>47,48</sup> Furthermore, two peaks at G and H were observed in the XANES spectrum coinciding with the  $\text{ZnCo}_2\text{O}_4$  sample, which can be attributed to the existence of multi-scattering effects.

To facilitate a comprehensive quantitative analysis of the local atomic structure of the  $\text{MCo}_2\text{O}_4$  nanomaterials, the EXAFS fitting in R-space was conducted.<sup>49</sup> The experimental EXAFS data in R-space in the range of  $1.0$  to  $5.0\text{ Å}$  with Hanning window and  $k$  range of  $3.0\text{ Å}^{-1}$  were analyzed to the best fit. The initial four high-ranking single scattering paths of Co–O and M–Co bond pairs were included in the fit. The passive electrons reduction factor  $S_0^2$  and energy shift  $E_0$  were set similarly for all the paths in the fit, and the mean-square relative displacement  $\sigma^2$  and interatomic distance  $R$  were refined relatively to get the best fit result.

Fig. 6 plots  $k^3$ -weighted EXAFS with the best fit, and the FT, respectively. The fit parameters with details are listed in Table 1. The FT analysis of spinel  $\text{FeCo}_2\text{O}_4$  structure shows a strong peak around  $1.500\text{ Å}$  assigned to the Fe–O<sub>1</sub> ( $2.239\text{ Å}$ ) coincides with T<sub>d</sub>  $\text{Fe}^{2+}$  and Fe–O<sub>2</sub> ( $1.963\text{ Å}$ ) assigned to O<sub>h</sub>  $\text{Fe}^{3+}$ . The Fe–Co<sub>1</sub> and Fe–Fe<sub>1</sub> bonds are observed near the  $3\text{ Å}$  which reveals the  $\text{Co}^{2+}$  cations are substituted by  $\text{Fe}^{2+}$  cations in the spinel  $\text{Co}_3\text{O}_4$  structure ( $\text{FeCo}_2\text{O}_4$ ). The Fe–Co<sub>1</sub> can be resolved to O<sub>h</sub>  $\text{Fe}^{3+}$  and



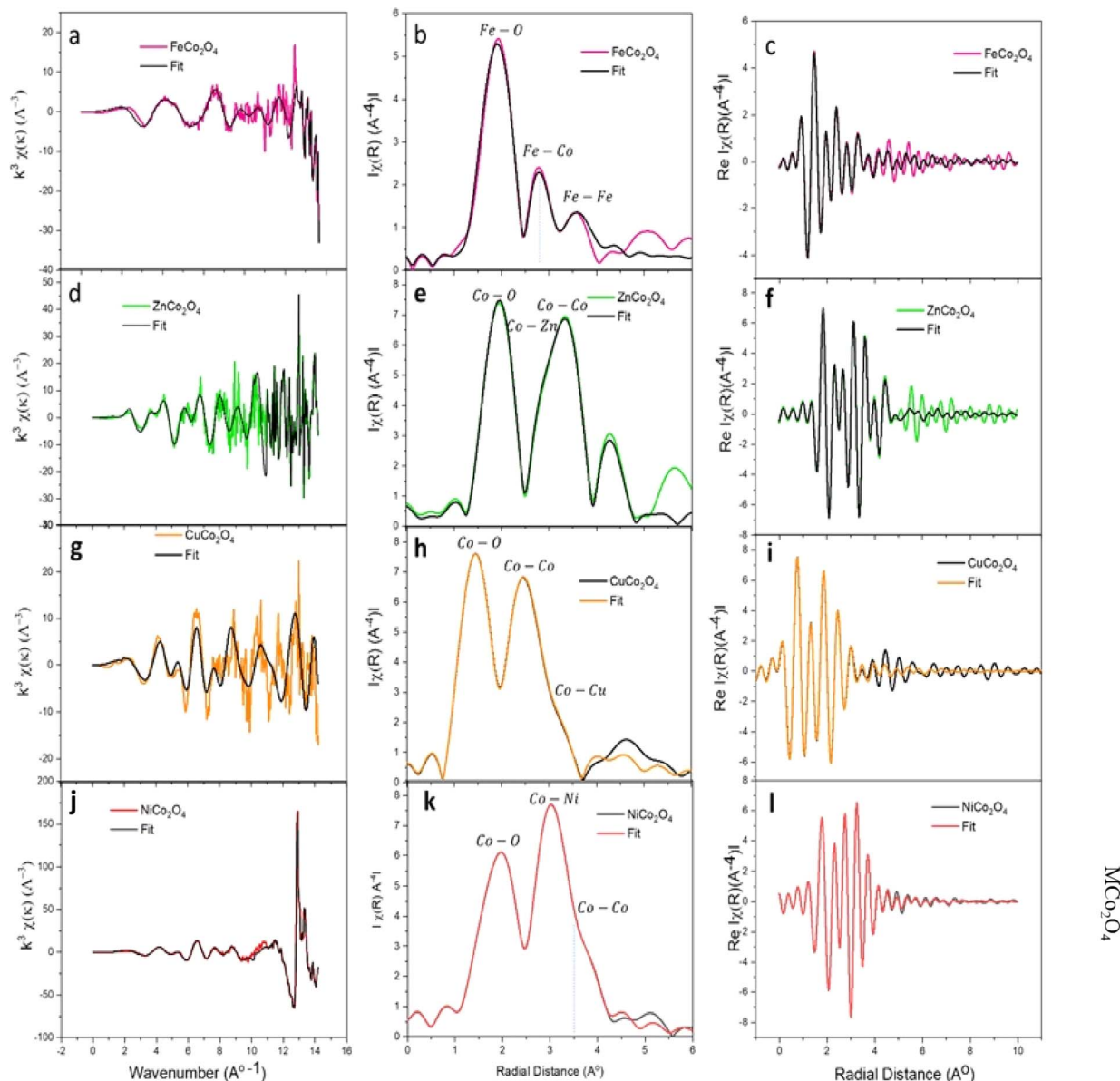


Fig. 6  $k^3$ -weighted EXAFS data with the best fit from Co and Fe K-edge absorption, FT, and the Re (FT) of the EXAFS data, respectively for (a–c)  $\text{FeCo}_2\text{O}_4$ , (d–f)  $\text{ZnCo}_2\text{O}_4$ , (g–i)  $\text{CuCo}_2\text{O}_4$  and (j–l)  $\text{NiCo}_2\text{O}_4$  samples.

$\text{T}_\text{d}$   $\text{Co}^{2+}$  sites. According to the reported data, the Fe, Cu, and Ni cations exhibit a tendency to occupy the octahedral sites ( $\text{O}_\text{h}$ ) and leave tetrahedral ( $\text{T}_\text{d}$ ) sites in spinel  $\text{Co}_3\text{O}_4$ .<sup>50</sup> On the other side, the  $\text{Co}^{2+}$  ions in the  $\text{Co}_3\text{O}_4$  compound are substituted by  $\text{Zn}^{2+}$  ions, which exhibit tetrahedral symmetry ( $\text{T}_\text{d}$ ), leading to the formation of  $\text{ZnCo}_2\text{O}_4$ .<sup>46</sup> Interestingly, the  $\text{ZnCo}_2\text{O}_4$  tends to form a spinel structure as the  $\text{Zn}^{2+}$  occupy the tetrahedral sites ( $\text{T}_\text{d}$ ) and leaving the  $\text{Co}^{3+}$  at octahedral sites ( $\text{O}_\text{h}$ ).<sup>51</sup> The crystal  $\text{ZnCo}_2\text{O}_4$  has a spinel structure ( $\text{A}^+\text{Co}_2^{3+}\text{O}_4$ , where, A is tetrahedral and B is octahedral sites) closely similar to the  $\text{Co}_3\text{O}_4$  structure.<sup>51</sup> Indeed, the FT shows  $\text{Co}-\text{O}_1$  (1.966 Å) interaction, which is characteristic of  $\text{O}_\text{h}$   $\text{Co}^{3+}$ . Also, the  $\text{Co}-\text{Zn}_1$  bond suggested  $\text{T}_\text{d}$   $\text{Zn}^{2+}$  and  $\text{O}_\text{h}$   $\text{Co}^{3+}$  in the spinel structure of  $\text{ZnCo}_2\text{O}_4$ . The  $\text{Co}-\text{O}_1$  and  $\text{Co}-\text{Co}_1$  own octahedral symmetry. This finding shows a good agreement with the previous reports that

confirmed the  $\text{CoO}_6$  structure has octahedral symmetry, whereas the  $\text{CoO}_4$  exhibits tetrahedral symmetry.<sup>52</sup> Furthermore, the results imply that the  $\text{Zn}^{2+}$  cations have a tendency to occupy active sites characterized by a low oxidation state, whereas  $\text{Co}^{3+}$  cations are left in octahedral locations. It is clear that  $\text{T}_\text{d}$   $\text{Zn}^{2+}$  and  $\text{O}_\text{h}$   $\text{Co}^{3+}$  ions were presented in the crystalline structure of the  $\text{ZnCo}_2\text{O}_4$  spinel structure.

Moreover, the FT first peak at 1.900 Å interatomic distance in spinel  $\text{CuCo}_2\text{O}_4$  structure corresponds to the  $\text{Co}-\text{O}_1$  (1.917 Å) of  $\text{O}_\text{h}$   $\text{Co}^{3+}$  and  $\text{Co}-\text{O}_2$  (2.058 Å) of  $\text{T}_\text{d}$   $\text{Co}^{2+}$ . The results in accordance with the previous reports.<sup>51,53</sup> The FT peak at 3.200 Å is correlated to  $\text{Co}-\text{Co}_1$  (3.237 Å) and  $\text{Co}-\text{Cu}_1$  (3.462 Å) bond interactions. It has been reported that the  $\text{Co}-\text{Co}$  interactions can be found in  $\text{O}_\text{h}$  and  $\text{T}_\text{d}$  as  $\text{Co}^{3+}-\text{Co}^{3+}$  (2.85 Å),  $\text{Co}^{3+}-\text{Co}^{2+}$  (3.346 Å), and  $\text{Co}^{2+}-\text{Co}^{2+}$  (3.495 Å).<sup>54</sup> Therefore, the  $\text{Co}-\text{Co}_1$



**Table 1** EXAFS fitting parameters, including coordination number (*N*), mean coordination shell radii (*R*), mean square relative displacements (MSRDs) or Debye–Waller factor ( $\sigma^2$ ), amplitude reduction factor ( $S_0^2$ ), photoelectron energy ( $E_0$ ) and goodness of the fit ( $R_{\text{factor}}$ ) for the  $\text{MCo}_2\text{O}_4$  binary metal oxides

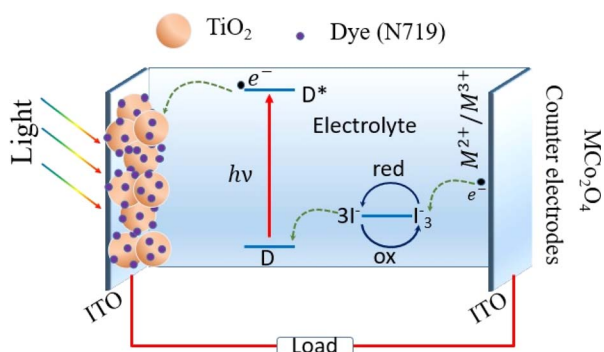
Sample	Bond type	<i>N</i>	<i>R</i> (Å)	$\sigma^2$ (Å <sup>2</sup> )	$S_0^2$	$E_0$ (eV)	$R_{\text{factor}}$
$\text{CuCo}_2\text{O}_4$	Co–O <sub>1</sub>	2	1.917 ± 0.010	0.0023 ± 0.0044	1	0.530	0.1057
	Co–O <sub>2</sub>	2	2.058 ± 0.091	0.0147 ± 0.0423	1	0.530	0.1057
	Co–Co <sub>1</sub>	2	3.237 ± 0.150	0.0094 ± 0.0057	1	0.530	0.1057
	Co–Cu <sub>1</sub>	4	3.462 ± 0.067	0.0066 ± 0.0087	1	0.530	0.1057
$\text{NiCo}_2\text{O}_4$	Co–O <sub>1</sub>	2	1.912 ± 0.017	0.0009 ± 0.0020	1	0.679	0.0103
	Co–O <sub>2</sub>	4	1.940 ± 0.174	0.0238 ± 0.0072	1	0.679	0.0103
	Co–Ni <sub>1</sub>	4	2.835 ± 0.042	0.0037 ± 0.0088	1	0.679	0.0103
	Co–Co <sub>1</sub>	2	2.988 ± 0.078	−0.0015 ± 0.0099	1	0.679	0.0103
$\text{ZnCo}_2\text{O}_4$	Co–O <sub>1</sub>	4	1.966 ± 0.036	0.0045 ± 0.0023	1	0.250	0.0571
	Co–O <sub>2</sub>	6	3.808 ± 0.166	0.0045 ± 0.0268	1	0.250	0.0571
	Co–Zn <sub>1</sub>	4	3.197 ± 0.058	0.0057 ± 0.0038	1	0.250	0.0571
	Co–Co <sub>1</sub>	6	3.439 ± 0.234	0.0001 ± 0.0303	1	0.250	0.0571
$\text{FeCo}_2\text{O}_4$	Fe–O <sub>1</sub>	2	2.239 ± 0.173	0.0056 ± 0.027	1	0.527	0.0320
	Fe–O <sub>2</sub>	4	1.963 ± 0.105	0.0045 ± 0.0054	1	0.527	0.0320
	Fe–Co <sub>1</sub>	4	3.224 ± 0.252	0.0006 ± 0.0123	1	0.527	0.0320
	Fe–Fe <sub>1</sub>	2	3.409 ± 0.266	−0.0015 ± 0.012	1	0.527	0.0320

interactions in spinel  $\text{CuCo}_2\text{O}_4$  assigned to O<sub>h</sub>  $\text{Co}^{3+}$  and T<sub>d</sub>  $\text{Co}^{2+}$ . Moreover, the Co–Cu<sub>1</sub> bridges the T<sub>d</sub>  $\text{Cu}^{2+}$  and T<sub>d</sub>  $\text{Co}^{2+}$ .

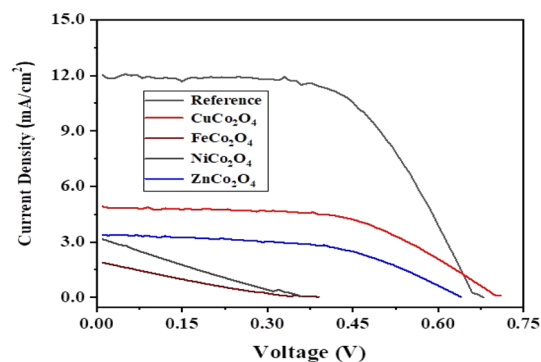
The above-reported XANES (Fig. 5b) pre-edge of  $\text{NiCo}_2\text{O}_4$  suggested the presence of T<sub>d</sub>  $\text{Co}^{2+}$  symmetry.<sup>55</sup> It can be preliminarily concluded that, the  $\text{NiCo}_2\text{O}_4$  is close to the spinel  $\text{Co}_3\text{O}_4$  structure and the oxidation state for both is 8/3 as oxidation state corresponding to the presence of O<sub>h</sub>  $\text{Ni}^{3+}$ .<sup>56</sup> The FT analysis of  $\text{NiCo}_2\text{O}_4$  reveals a peak at the lowest interatomic distance of 1.94 Å assigned to Co–O<sub>1</sub> of O<sub>h</sub> ( $\text{Co}^{3+}\text{O}_6$ ) and Co–O<sub>2</sub> of T<sub>d</sub> ( $\text{Co}^{2+}\text{O}_4$ ).<sup>57</sup> The next FT peak at 2.9 Å corresponds to Co–Co<sub>1</sub> (2.988 Å) and 4Co–Ni<sub>1</sub> (2.835 Å) interactions. It's evident the Co–Co<sub>1</sub> is characteristic of O<sub>h</sub>  $\text{Co}^{3+}$  and the Co–Ni<sub>1</sub> coincides characteristic of O<sub>h</sub>  $\text{Co}^{3+}$  and the Co–Ni<sub>1</sub> coincides with O<sub>h</sub>  $\text{Co}^{3+}$  and O<sub>h</sub>  $\text{Ni}^{3+}$ . In general, the Co–O interatomic distances at T<sub>d</sub> or O<sub>h</sub> sites are shorter than M–O distances which is correlated with a small atomic radius of  $\text{Co}^{3+}$  in comparison with  $\text{M}^{2+}$ . It is obvious that the Co–O<sub>1</sub> and Co–O<sub>2</sub> in  $\text{ZnCo}_2\text{O}_4$  are longer compared to other spinel structures. It is worth noting that, the interatomic distances of M–Co introduced in Table 1 are observed as Co–Cu > Co–Fe > Zn–Co > Co–Ni.

The working mechanism of DSSCs in this study, as illustrated in Fig. 7, involves several key components and processes.

The  $\text{TiO}_2$  nanoparticle-decorated ITO-coated photoanode serves as the light-harvesting layer. When light is absorbed by the sensitizer dye (here N719), it excites electrons from the dye into the conduction band of the  $\text{TiO}_2$ . These photo-generated electrons then move through the  $\text{TiO}_2$  nanoparticles and are collected at the ITO substrate, flowing into the external circuit to generate electric current. The oxidized dye molecules are regenerated by electrons from the iodide ( $\text{I}^-$ ) in the electrolyte, which is subsequently oxidized to tri-iodide ( $\text{I}_3^-$ ). The tri-iodide ions diffuse towards the spinel cobalt-based metal oxide  $\text{MCo}_2\text{O}_4$  thin film counter electrodes, where they are reduced back to iodide ions, completing the circuit. This process is facilitated by the high electrocatalytic activity of the  $\text{MCo}_2\text{O}_4$  counter electrodes, which efficiently catalyzes the reduction of tri-iodide. The high surface area and conductivity of the  $\text{MCo}_2\text{O}_4$  thin films can play an important role in efficient electron transfer and low charge transfer resistance, contributing to the high performance of the DSSCs. Additionally, the chemical and thermal stability of  $\text{MCo}_2\text{O}_4$  provides durability and long-term performance stability, making it an excellent choice for counter electrodes in high-performance DSSCs.



**Fig. 7** Schematic diagram of  $\text{MCo}_2\text{O}_4$  counter-electrode-based DSSC.



**Fig. 8** Current density–voltage plots of DSSCs formed using Pt and  $\text{MnCo}_2\text{O}_4$ -based counter electrodes.



Table 2 Some photovoltaic parameters of the DSSCs fabricated using Pt and  $\text{MCo}_2\text{O}_4$ -based counter electrodes

DSSCs	$J_{\text{max}}$ $\text{mA cm}^{-2}$	$V_{\text{max}}$ mV	$J_{\text{sc}}$ $\text{mA cm}^{-2}$	$V_{\text{oc}}$ mV	FF	PCE %
$\text{CuCo}_2\text{O}_4$	4.23	550	4.80	705.8	56.1	1.90
$\text{FeCo}_2\text{O}_4$	0.99	150	1.96	401.8	18.8	0.15
$\text{NiCo}_2\text{O}_4$	1.67	160	3.25	364.9	22.6	0.27
$\text{ZnCo}_2\text{O}_4$	2.83	400	3.41	642.0	51.7	1.13
Pt	10.81	440	12.1	664.1	59.2	4.76

Fig. 8 shows current density–voltage ( $J$ – $V$ ) plots of the DSSCs fabricated using sensitized  $\text{MCo}_2\text{O}_4$  based counter electrodes in comparison with Pt-based one as reference solar cell under illumination of  $100 \text{ mW cm}^{-2}$ . Table 2 summarizes the obtained results and highlights significant differences among the examined thin films. As presented in Table 2, the DSSC with a counter electrode based on  $\text{CuCo}_2\text{O}_4$  nano-leave gives the best photovoltaic response with a  $J_{\text{max}}$  of  $4.23 \text{ mA cm}^{-2}$  and a  $V_{\text{max}}$  of 550 mV which results in 1.9% power conversion efficiency. It is also seen that the open circuit voltage ( $V_{\text{oc}}$ ) value of this device (705.8 mV) superior to the one for conventional DSSC with Pt electrode (664.1 mV). The second-best solar cell efficiency is reported as 1.13% for the DSSC obtained using  $\text{ZnCo}_2\text{O}_4$  hexagonal-like structures. The  $V_{\text{oc}}$  value of this device with 642.0 mV is very close to the cell with Pt electrode. The other two solar cells obtained from  $\text{NiCo}_2\text{O}_4$  nanosheets and  $\text{FeCo}_2\text{O}_4$  diamond-like structures have lower PCE values of 0.27 and 0.15%, respectively. The lower short-circuit current density ( $J_{\text{sc}}$ ) values observed in our study for DSSCs utilizing alternative counter electrodes, such as  $\text{CuCo}_2\text{O}_4$ ,  $\text{FeCo}_2\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4$ , and  $\text{ZnCo}_2\text{O}_4$ , compared to conventional Pt-based DSSCs. It suggests potential limitations in transport mechanisms associated with these materials. Factors such as differences in catalytic activity, electronic structure, and surface morphology may contribute to the reduced efficiency of photogenerated charge carriers and subsequent lower  $J_{\text{sc}}$  values. Similar studies have been performed for various metal oxides including binary metal oxides.<sup>58–60</sup> For instance, Kaya *et al.* hydrothermally sensitized  $\text{CuCrO}_2$  delafossite oxide nanoparticles to use them as photocathode in the fabrication of high efficient tandem p–n photoelectrochemical cells using  $\text{CuCrO}_2$  delafossite semiconductors as photocathodes coupling with traditional n-type  $\text{TiO}_2$  based photoanodes.<sup>59</sup> They reported the efficiency of solar cells between 1.67 and 2.33% for various annealing temperatures.

Considering the structural properties examined in this study across various spinel metal oxides, the samples consistently demonstrated high crystallinity, primarily in the cubic phase. Notably, the identification of active structural planes in these samples indicates a correlation between electrochemical activity and charge injection with these specific planes. For instance, the (311) plane was prominent in the  $\text{ZnCo}_2\text{O}_4$  structure, the (220) plane in  $\text{CuCo}_2\text{O}_4$ , both (311) and (220) planes in  $\text{NiCo}_2\text{O}_4$ , and the (220) plane in  $\text{FeCo}_2\text{O}_4$ . Furthermore, distinctive characteristics and morphologies were observed in the hexagonal structure of  $\text{ZnCo}_2\text{O}_4$  and the nanosheet morphology of  $\text{CuCo}_2\text{O}_4$ , which are thought to enhance the photocurrent and efficiency of DSSCs.

## Conclusions

The spinel cobalt-based metal oxides of  $\text{MCo}_2\text{O}_4$  (M: Ni, Cu, Fe, or Zn), were synthesized through the hydrothermal growth technique on ITO substrate to use them as counter electrodes in the fabrication of Pt free DSSCs. The oxides displayed a uniform and homogeneous surface morphology. Interestingly,  $\text{NiCo}_2\text{O}_4$  exhibits nanosheets,  $\text{FeCo}_2\text{O}_4$  displays diamond shapes,  $\text{CuCo}_2\text{O}_4$  shows nanoleaves, and  $\text{ZnCo}_2\text{O}_4$  presents a hexagonal shape. These morphologies exhibit unique structural features characterized by a significantly large surface area and the existence of surface defect sites to enhance chemical reactivity. To probe the local structure of the prepared samples, EXAFS data was carried out at Fe and Co K-edge. The absorption Co K-edge was close to the 7721.4 eV value reported in the literature. The Fe K-edge was 7125.53 eV for  $\text{FeCo}_2\text{O}_4$ . The pre-edge peak in XANES of the prepared samples suggested  $\text{Td Co}^{2+}$ . The shape of the XANES spectrum reveals the spinel structure of the obtained samples. The FT reveals a Co–O<sub>1</sub> coincides with O<sub>h</sub>  $\text{Co}^{3+}$  and Co–O<sub>2</sub> is characteristic for  $\text{Td Co}^{2+}$ . On the contrary, Fe–O<sub>1</sub> reveals  $\text{Td Fe}^{2+}$  and Fe–O<sub>2</sub> associated with O<sub>h</sub>  $\text{Fe}^{3+}$ . The interatomic distances evaluated from FT analysis of M–Co were observed as Co–Cu > Co–Fe > Zn–Co > Co–Ni. In addition, it is reported that these spinels cobalt-based binary metal oxides, especially  $\text{CuCo}_2\text{O}_4$  nanoleaves and  $\text{ZnCo}_2\text{O}_4$  hexagonal-like structures are promising candidates for the low cost and high efficient DSSCs with 1.9 and 1.13% power conversion efficiency values, respectively.

## Data availability

The data that support the findings of this study are available from the corresponding author, Bashar Aljawrneh, upon reasonable request. Researchers interested in accessing the data should contact Bashar Aljawrneh at b.aljawrneh@zuj.edu.jo.

## Author contributions

Abdelelah Alshanableh: conceptualization, investigation, methodology, data curation, writing – original draft, writing – review & editing. Yusuf Selim Ocak: conceptualization, investigation, methodology, data curation, writing – original draft, writing – review & editing. Bashar Aljawrneh: conceptualization, investigation, methodology, data curation, writing – original draft, writing – review & editing. Borhan Aldeen Albiss: supervision, investigation, review & editing, funding acquisition.



Khaled Shawakfeh: supervision, investigation, review & editing, funding acquisition. Latif U. Khane: investigation, methodology, data curation, writing – original draft. Messaoud Harfouch: investigation, methodology, data curation, writing – original draft. Saja Alrousan: investigation, methodology, data curation.

## Conflicts of interest

There are no conflicts to declare.

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