Structural, Magnetic and Dielectric Properties of Dy-doped \( \text{Co}_3\text{O}_4 \) Nanostructures for the Electrochemical Evolution of Oxygen in Alkaline Media

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ABSTRACT

In this study, spinel-type cobalt oxide (\( \text{Co}_3\text{O}_4 \)) and \( \text{Co}_{3-x}\text{Dy}_x\text{O}_4 \) (x = 0.04 and 0.05 molar ratio) nanoparticles were synthesized via combustion method at 700 °C. Crystallite nature, phase purity and thermal analysis of the prepared compounds were investigated by PXRD, FT-IR and TGA techniques. Structural analyses were performed by the FullProf program employing profile matching with constant scale factors. The results showed that the patterns had a main cubic structure with space group of Fd3m. The cell parameter data calculated by rietveld analysis showed that the cell parameters were nearly constant. The morphological and structural properties of the obtained materials were examined by FESEM and TEM images. Besides, the magnetic measurements of \( \text{Co}_3\text{O}_4 \) and \( \text{Co}_{3-x}\text{Dy}_x\text{O}_4 \) nanoparticles were performed by vibration sampling magnetometer (VSM). Coercivity (Hc) and remanent magnetization (Mr) were found to be reduced in Dy\(^{3+}\) doped \( \text{Co}_3\text{O}_4 \) while saturation magnetization (Ms) was increased moderately. The effect of dysprosium ion addition was also studied using cyclic voltammetry (CV) for the oxygen evolution reaction in an alkaline environment. The obtained data showed that the presence of Dy\(^{3+}\) exhibited a much higher oxygen evolution activity and lower over potential compared to \( \text{Co}_3\text{O}_4 \).

INTRODUCTION

In recent years, the production of transition metal oxides has attracted the attention of some research groups due to their special properties and envisioned applications in optics, magnetic materials and electronics [1-5]. Among the metal oxides, a great attention has been focused on the synthesis of spinel-type tricobalt tetraoxide (\( \text{Co}_3\text{O}_4 \)) which is important in Li-ion rechargeable batteries [6], anti-ferromagnetic p-type semiconductor, heterogeneous effective catalyst in chemical engineering and environmental purification [7-8], magnetic materials [9-10], electrochemical devices [11], etc. In \( \text{Co}_3\text{O}_4 \) or \( \text{CoCO}_2\text{O}_4 \) as \( \text{AB}_2\text{O}_4 \) spinel, the magnetic \( \text{Co}^{3+} \) (3d\(^7\)) cations are located in the tetrahedral sites and non-magnetic \( \text{Co}^{3+} \) (3d\(^6\)) cations have occupied the octahedral ones. In bulk crystalline form, \( \text{Co}_3\text{O}_4 \) renders antiferromagnetism whereas the nanosized \( \text{Co}_3\text{O}_4 \) shows weak ferromagnetism or superparamagnetism [5]. Until now, several methods such as hydrothermal [12,13], sol–gel [14], chemical spray pyrolysis [15], microemulsion [16], chemical vapor deposition [17], thermal decomposition of cobalt precursors [18] sonochemical route [19], microwave irradiation [20], co-precipitation [21], and mechanochemical processing [22] have been reported for the synthesis of \( \text{Co}_3\text{O}_4 \). But most of these methods require expensive or special instruments and need

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harsh conditions. Combustion method is known as an attractive technique for the synthesis of different oxides, including perovskites, ferrites and zirconia [23-27]. Moreover, the combustion of the corresponding complexes is one of the least expensive and simplest methods for preparing transition metal oxides nanoparticles with high purity [28–31].

In this paper, we present a facile combustion method for the synthesis of spinel-type Co$_3$O$_4$ nanoparticles using a classical complex, [Co(acac)$_3$]. So far, several metals have been proposed for the synthesis of doped cobalt oxides. For example, Jang et al. [32] prepared Mn-doped Co$_3$O$_4$, Jeong et. al. [33] reported $\alpha$-MnO$_2$ doped Co$_3$O$_4$, and Rahman et. al. [34] reported Cr-doped Co$_3$O$_4$. Lanthanide-doped cobalt oxides have also been occasionally reported. Herein we report the synthesis of Dy$^{3+}$-doped Co$_3$O$_4$ nanosstructure by combustion of [Co(acac)$_3$]. The morphology, structure, thermal behavior and magnetic properties of the as prepared Co$_3$O$_4$ and Dy$^{3+}$-doped Co$_3$O$_4$ nanostructures were investigated by SEM, TEM, XRD, FT-IR spectra, cyclic voltammetry (CV), TGA and VSM.

**EXPERIMENTAL**

**Materials and Characterization techniques**

All the chemicals and solvents were of analytical grade and were used without further purifications. Fourier transform infrared (FT-IR) spectrum were measured by a FT-IR SHIMADZU spectrophotometer, with KBr pellet technique in the wavelength range from 4000-400 cm$^{-1}$ to measure the structural components. The crystallographic information and phase purity of the samples was obtained with the X-ray powder diffraction (XRD) using Bruker D8000 Germany in a scanning range of 2θ = 10–90°. The morphological, structural and particle size distribution of the nanostructures of Co$_3$O$_4$ were carried by the Hitachi FESEM model S-4160 field emission scanning electron microscope (FESEM) and a transmission electron microscopy (TEM, Philips-CM300). Thermal analysis (TGA) curve were recorded with a STA PT 1600- Linseis(Germany) using a heating rate of 5 °C.min$^{-1}$ in air atmosphere. Also, magnetic measurements were carried out with a vibrating sampling magnetometer (VSM, Model 7400- LakeShore). All electrochemical tests were done by a Metrohm instrument, Model 797 VA processor, or an Autolab potentiotstat-galvanostat, Model PGSTAT302. A platinum wire as a counter electrode, an Ag/AgCl (3.0 mol L$^{-1}$ KCl) reference electrode and a modified or unmodified glassy carbon electrode (GCE) as a working electrode were placed in a cell containing electrolyte, and then it was used as a conventional three-electrode system for all the electrochemical experiments. All the potentials reported in this work are vs. Ag/AgCl (3.0 mol L$^{-1}$ KCl).

**Preparation [Co(acac)$_3$] complex as a precursor**

The complex was synthesized relevant to the general synthetic method in the literature. In a typical synthesis procedure, 0.38 g (0.0015mmol) of Co(CH$_3$COO)$_2$.4H$_2$O was dissolved into 5 mL distilled water and was heated to about 90°C using a hot water bath with ongoing stirring, then 3 mL of acetylacetone was added. While maintaining the reaction temperature around 90°C, 4.5 mL of 35% H$_2$O$_2$ was added drop-wise, using a dropping pipette during 20 min. The reaction flask was covered by a watch glass during the hydrogen peroxide addition. Stirring was retained throughout the addition and then for a further 15 minutes. After this step, the reaction flask was cooled in an ice-water bath for 20 minutes. Dark green precipitate was filtered under vacuum, washed with distilled water, vacuum dried for10 minutes and then dried in the oven at 100 °C. Yield: 75%. FT-IR: ѵ$_{\text{max}}$ cm$^{-1}$ (KBr): 1565 (w, C-H), 1573 (C=O), 1512 (C=C).

**Preparation of Co$_3$O$_4$ nanoparticles**

An appropriate amount of the [Co(acac)$_3$] complex powder (2g) as the precursor for the synthesis of Co$_3$O$_4$ ($S_0$) was transferred into a crucible. To prevent the possibility of dispersion, it was turned gel-like with a small amount of distilled water. The crucible containing the complex was heated at 700 °C for 8h. The black powder
obtained from the calcination was collected for characterization. Yield: 85%. FT-IR: $v_{\text{max}}$ cm$^{-1}$ (KBr): 665 (Co-O), 576 (Co-O), 1512 (C=C).

**Preparation of Co$_3$Dy$_x$O$_4$ nanoparticles**

Proper molar amounts of [Co(acac)$_3$] (1.96, 1.95) and Dy$_2$O$_3$ (0.04 ($S_1$) and 0.05 ($S_2$), respectively), were added to a crucible. It was then heated at 700 °C for 8h. The obtained sample powder (Co$_{3-x}$Dy$_x$O$_4$) was collected for characterization and for comparison with the pure cobalt oxide.

**Preparation of the electrodes**

The GCE was polished mechanically with 5 µm alumina slurry on a polishing cloth. Afterwards, the electrode was washed ultrasonically in a mixture of ethanol/distilled water solution (1:1 V/V) for 10 min and dried in the room temperature.

To deposit Co$_3$O$_4$ and Co$_{1.96}$Dy$_{0.04}$O$_3$ on the electrode, a relative stable suspension were obtained by ultrasonically dispersing of the synthesized powders (0.10 mg) in 10 mL distilled water. Then, 5.0 µL of the suspension was dropped on the electrode and allowed to dry in the air at room temperature. Finally, 5 µL of 1% wt. Nafion solution was dropped onto the electrode to increase the adhesion of the coatings to the surface. The Co$_3$O$_4$/GCE and Co$_{1.96}$Dy$_{0.04}$O$_3$/GCE, were obtained using the above mentioned procedure.

**RESULTS AND DISCUSSION**

**X-ray diffraction studies**

Fig. 2. shows the XRD pattern of [Co(acac)$_3$] complex. All diffraction peaks in this XRD pattern matched very good with those reported in the literature for the pure [Co(acac)$_3$] complex with JCPDS Card no. 24-1627. XRD technique was used to check the crystallinity and phase purity of the as-prepared Co$_3$O$_4$ (Fig. 3 (a)). Our analysis revealed that all diffraction peaks were sharp and slender, which insinuate the excellent degree of crystallinity. The XRD patterns of the sample indicated obvious diffraction peaks corresponding to 2θ = 19.01°, 31.28°, 36.87°, 38.59°, 44.82°, 55.68°, 59.4° and 65.25° which were assigned to the (111), (220), (311), (222), (400), (422), (511) and (440) crystalline planes, respectively. Also, Structural analysis was done by the FullProf program by employing profile matching with constant scale factor. Red bars are observed intensities in which obtained from the diffraction data. Black ones are calculated data. Blue one is the difference: Yobs-Ycalc. The bars below indicate the Bragg reflections. Since we have two lines of bars, it means there are two phases. The upper one is corresponded to Co$_3$O$_4$ and the below one is due to Dy$_2$O$_3$. For comparison, we included the impurity phase in both $S_1$ and $S_2$ to confirm that the impurity phase is apparent in $S_2$. The obtained data confirmed the synthesis of Face Centered Cubic phase spinel Co$_3$O$_4$ crystalline structure with lattice parameters of about a = b = c = 8.08 Å according to the JCPDS Card no. 43-1003 and space group Fd3m [38]. This result confirmed the complete decomposition of precursor [Co(acac)$_3$] into Co$_3$O$_4$ crystal phase at 700 °C. Preliminary structural investigation of all doped samples in Co$_{3-x}$Dy$_x$O$_4$ were determined by analyzing the X-ray diffraction patterns. Fig. 3b shows the XRD patterns of Co$_{3-x}$Dy$_x$O$_4$ in different molar ratio (x = 0.04 and 0.05) indicates that the positions of characteristic
peaks for the doped sample from \( x = 0.04 \) is consistent with those of undoped cobalt oxide in Fig. 3(a). This indicates that dysprosium ions have been well accommodated into cobalt lattice sites without grable crystal symmetry. According to Fig. 3c, increasing the amount of dopant Dy\(^{3+}\) ions to \( x = 0.05 \) shows diffraction lines (red bars) at \( 2\theta \approx 28.98^\circ, 43.28^\circ \) which could be assigned to the \( (222) \) and \( (134) \) crystalline planes of excess Dy\(_2\)O\(_3\). Only a small fraction of the total amount of Dy\(^{3+}\) ions goes into the cobalt sites and additional amount may be on the grain boundaries of the nanocrystals or stay on the surface [40]. Therefore, the maximum amount of doped ion is 0.05 mmol.

Table 1. Scherrer data information for pure Co\(_3\)O\(_4\) nanomaterials obtained after 8 h at 700 \( ^\circ \)C in \( x = 0.0, 0.04 \) and 0.05 mmol.

<table>
<thead>
<tr>
<th></th>
<th>( S_1 )</th>
<th>( S_2 )</th>
<th>( S_3 )</th>
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<tr>
<td>( 2\theta )</td>
<td>36.8664</td>
<td>36.8903</td>
<td>36.9121</td>
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<tr>
<td>FWHM</td>
<td>0.23554</td>
<td>0.23334</td>
<td>0.23251</td>
</tr>
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<td>( \beta )</td>
<td>0.00410</td>
<td>0.00407</td>
<td>0.004056</td>
</tr>
<tr>
<td>( \cos(\theta) )</td>
<td>0.9487</td>
<td>0.9486</td>
<td>0.9486</td>
</tr>
<tr>
<td>( D ) (nm)</td>
<td>36</td>
<td>36</td>
<td>36</td>
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<tr>
<td>Cell parameter(( \AA ))</td>
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<td>8.084304</td>
<td>8.071710</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>2.66</td>
<td>1.86</td>
<td>1.37</td>
</tr>
</tbody>
</table>

Table 1 shows the average particle size of the nanostructures calculated using the Scherrer’s equation [39]:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

Where \( D \), \( \lambda \), \( \theta \) and \( \beta \) are the average crystalline size, the X-ray wavelength of Cu K\( \alpha \), the Bragg’s diffraction angle and the full width at half maximum (FWHM) of the diffraction peak respectively.

Besides, Table 1 shows cell volume and reduced
average crystallite sizes of \(\text{Co}_{3-x}\text{Dy}_x\text{O}_4\) in different molar ratios \((x = 0.04\) and \(0.05\)). Table 1. indicates that the added \(\text{Dy}^{3+}\) has prevented the increasing the crystallite size. The observed very little decreasing the cell volume and very little increasing average crystallite size is due to the difference in the ionic radius of dysprosium and cobalt ions (ionic radius of \(\text{Dy}^{3+} = 0.91\ \text{A}°\), \(\text{Co}^{3+} = 0.65\ \text{A}°\) and \(\text{Co}^{2+} = 0.61\ \text{A}°\)) [41]. The \(\chi^2\) values obtained from the rietveld analyses show the goodness of the analysis.

**FTIR spectra**

Fig. 4. shows the FT-IR spectra of the \([\text{Co(acac)}_3]\) complex and its calcination product at 700 °C. The spectrum of \([\text{Co(acac)}_3]\) shows the characteristic absorption band of the resonant \(\text{C}=\text{O}\) vibration at 1573 cm\(^{-1}\). For the calcined sample (\(\text{Co}_3\text{O}_4\)), the obtained results matched well with the spinel-type \(\text{Co}_3\text{O}_4\) structure. Inspection of this spectrum revealed the presence of only two characteristic bands of the cobalt oxide at 576 cm\(^{-1}\) (\(\nu_1\)) and 665 cm\(^{-1}\) (\(\nu_2\)) which were due to the \(\text{M-O}\) vibrations, confirming complete decomposition of the \([\text{Co(acac)}_3]\) complex to the cobalt oxide and the formation of spinel \(\text{Co}_3\text{O}_4\) [12,35-36]. The \(\nu_1\) band is characteristic of \(\text{Co}^{3+}\) vibration in the octahedral site formed by the oxide ions and the \(\nu_2\) band is assigned to the \(\text{Co}^{2+}\) vibrations in the tetrahedral sites, in the spinel lattice [37].

**Field emission scanning electron microscope (FESEM)**

Fig. 5. shows the FESEM images of spinel \(\text{Co}_3\text{O}_4\) prepared via the combustion of \([\text{Co(acac)}_3]\) complex without using fuel. As could be seen, the prepared \(\text{Co}_3\text{O}_4\) nanoparticles exhibited a spherical morphology with holes randomly distributed among them and the pore sizes of about 50-100 nm with high density.

Figs. 6-7 display the FESEM images of the \(\text{Dy}^{3+}\)-doped \(\text{Co}_3\text{O}_4\) \((x = 0.04\) and \(0.05\ \text{mmol},\) respectively). As could be seen from Fig. 6, the pores have multigonal structure and pore sizes are about 50-150 nm. The particles of the porous are homogeneous, so porous became homogeneous too. According to Fig. 7, by doping \(\text{Dy}^{3+}\) in \(\text{Co}_3\text{O}_4\) structure, porous layer particles and some particles have been seen so that porous in Fig. 7a and b have two small sizes with a medium size about 30-50 nm and large size with a medium size about 200 nm.

**Transmission electron microscopy (TEM)**

The physical nature and exact size of the particles of the \(\text{Co}_3\text{O}_4\) were determined by TEM. Fig. 8 shows TEM images of the as prepared \(\text{Co}_3\text{O}_4\) nanoparticles with fusiform-like morphology and multigonal particles. Moreover, the particles of tricobalt tetroxide have homogeneous and uniform distribution in the powder sample. For obtaining the exact size of the particles, manual analysis has been done which is shown in Fig. 8. In this plot, the particle size is about 100 nm. Fig. 10 shows TEM images of the \(\text{S}_2\). As is seen in Fig. 11, the particles sizes are in the range of 14 nm to 18 nm. According to the TEM image, it could be recognized that the used preparation method is
suitable to obtain the nanoparticles of Co$_3$Dy$_x$O$_{4-x}$. Low Dy$^{3+}$ amount is recommended in Co$_3$O$_4$ synthesis to avoid agglomeration of the particles, higher homogeneity and to obtain powder with smaller size in comparison with undoped sample.

Elemental map analysis (Fig. 12) was used for investigation of elemental distributions in synthesized Co$_{2.96}$Dy$_{0.04}$O$_4$. It can be seen from fig. 9 that Dy, Co and O in Co$_{2.96}$Dy$_{0.04}$O$_4$ are uniformly distributed in this work. Also, Fig. 13 shows the EDS elemental analysis for Co$_{2.96}$Dy$_{0.04}$O$_4$. Results show the presence of 54.99 at.% O, 1.87 at.% Dy, 3.23 at.% C and 39.91 at.% Co, for the Co$_{2.96}$Dy$_{0.04}$O$_4$ that confirm MAP analysis investigation. Presence of C

Fig. 5. FESEM images of Co$_3$O$_4$.

Fig. 6. FESEM images of Co$_{3-x}$Dy$_x$O$_4$ (x= 0.04).
Thermal analysis

The TG thermogram of nano-Co$_3$O$_4$ with heating rate of 5 °C.min$^{-1}$ in air atmosphere as carrier gas is shown in Fig. 14. The TG curve shows two weight loss (WL) steps from ambient temperature till 1000 °C. In the first weight loss step, the TGA showed a gradual weight loss (8%) up to around 160 °C with the temperature rise which corresponds to loss of structural water [42]. The seconds weight loss step occurs at the 890-920 °C temperature range with 10% weight loss, which is due to the decomposition of Co$_3$O$_4$ into CoO and O$_2$ according to the following equilibrium [43]:

$$\text{Co}_3\text{O}_4 \rightarrow \text{CoO} + \frac{1}{2}\text{O}_2$$

Electrochemical impedance spectroscopy

The electrical conductivity effects of the synthesized nanoparticles were investigated using EIS. Electron transfer resistance, $R_{ct}$, is an important factor for this goal. The semicircle portion at higher frequencies corresponded to the electron
transfer limited process for a conductive surface or electroactive compound. Fig. 15 shows the impedance plots for (a) GCE, (b) Co$_3$O$_4$/GCE, and (c) Co$_{1.96}$Dy$_{0.04}$O$_3$/GCE in 1.0 mM [Fe(CN)$_6$]$^{3-}$/$^{4-}$ (1:1) solution in 0.1 M KCl. It is evident from the EIS data, at a surface of GCE modified with Co$_3$O$_4$, the electron transfer resistance was at its minimum value that is relative to the high conductivity effect of Co$_3$O$_4$ at the surface of electrode. Also, the $R_{ct}$ for GCE modified with Co$_{1.96}$Dy$_{0.04}$O$_3$ is high compared to Co$_3$O$_4$ that shows doping of Dy$^{3+}$ reduces electrical conductivity of Co$_3$O$_4$.

**Magnetic measurements**

The magnetic characterization of the prepared pure and doped Co$_3$O$_4$ was examined using...
vibration sampling magnetometer (VSM). The magnetic behavior of the samples in the M-H (M- magnetization (memu/g) and H- magnetic field (Gauss)) curve are shown in Fig. 16(a-b), respectively. The $\text{Co}_3\text{O}_4$ nanoparticles and $\text{Co}_{3-x}\text{Dy}_x\text{O}_4$ showed a weak ferromagnetic nature in which, a tiny hysteresis loop can be seen for pure $\text{Co}_3\text{O}_4$. In general, bulk $\text{Co}_3\text{O}_4$ has normal spinel structure with antiferromagnetic exchange between ions occupying the tetrahedral A (high spin Co$^{2+}$) sites and the octahedral B (low spin Co$^{3+}$) sites [44]. It is known that for bulk antiferromagnetic materials, zero net magnetization is due to the complete compensation of sublattice magnetizations. Hence, the change from an antiferromagnetic behavior for bulk $\text{Co}_3\text{O}_4$ to a weak ferromagnetic behavior for $\text{Co}_3\text{O}_4$ nanoparticles can be attributed to the uncompensated surface spins and/or finite size effects of the tericobalt tetraoxide nanoparticles [45-47]. For the weak ferromagnetic behavior of the antiferromagnetic nanostructured material, different models have been proposed, such as $\text{Co}_3\text{O}_4$ mesoporous [48], CoO thin layers [49], $\text{Co}_3\text{O}_4$ nanoparticles [9,10, 50-53] and ferromagnetic behavior in cobalt oxide nanoparticles based on finite size effect [54]. The Dy$^{3+}$ ions substituted cobalt ions in both positions and have changed the magnetic interactions between the two sites; this change can cause magnetic parameters change compared to the pure $\text{Co}_3\text{O}_4$. With doping the dysprosium oxide, remanent magnetization (Mr) and coercive force (Hc) has been reduced, which

Fig. 13. EDS analysis of the powders $\text{Co}_{1.96}\text{Dy}_{0.04}\text{O}_3$.

Fig. 14. TG thermograms of $\text{Co}_3\text{O}_4$ nanoparticles in air atmosphere in the temperature range from 25–1000 °C and heating rate of 5 °C min$^{-1}$.
is shown in Table 2. Also, the hysteresis loop is not observed in doped sample.

* Catalytic activity for oxygen evolution

Oxygen evolution reaction (OER) is one of the most important processes in various electrochemical devices. Spinal-type Co$_3$O$_4$, an inexpensive material, has shown high activity and long term performance for OER in alkaline electrolyte. Therefore, many studies have been
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devoted to the improvement of the composition and structure of Co₃O₄ to increase of OER efficiency. The doping of various metals in Co₃O₄ structure is one way that is employed to increase the performance of Co₃O₄.

The effect of dysprosium doping on the electrocatalytic activity of Co₃O₄ was studied using cyclic voltammetry (CV) for the OER in alkaline media. Fig. 17 shows that the presence of dysprosium increases the current of the oxygen evolution. At a fixed potential of 1.2 V, current value for Co₂.₉₆Dy₀.₀₄O₄/GCE is 1.79 mA, which is about 1.5 times higher than 1.22 mA for Co₃O₄/GCE. Moreover, it is found that at a fixed current of 1.50 mA, the potential is 1.16 V for Co₂.₉₆Dy₀.₀₄O₄/GCE and 1.24 V for Co₃O₄/GCE, i.e. the overpotential is improved 0.08 V by doping dysprosium. The performance improvement of OER by dysprosium may be due to an increase in electrical conductivity, as evidenced using EIS in section 3.6.

CONCLUSIONS

In this paper, nanosized Co₃O₄ and Dy³⁺-doped Co₃O₄ nanoparticles were successfully prepared by the combustion of [Co(acac)₃] complex at 700 ºC. FT-IR and X-ray diffraction (XRD) investigates confirmed the Co₃O₄ and Co₃₋ₓDyₓO₄ formation and showed the purity of the compounds. TG curve showed a reasonable thermal behavior of cobalt oxide. Surface morphology and particle size distribution of the synthesized materials investigated by FESEM and TEM images, also confirmed dysprosium role in better distribution of nanoparticles and in particle growth reduction. From this images, the spherical morphology was observed with holes randomly distributed among them in the Co₃O₄, while in the Co₃₋ₓDyₓO₄ the pores have multigonal structure. Porous layer particles and doping of Dy³⁺ ions promotes improved morphology of Co₃₋ₓDyₓO₄ nanostructures with higher uniformity compared to pure Co₃O₄. Weak ferromagnetic behavior was observed in the compounds using the VSM measurements. A small hysteresis loop was observed for pure Co₃O₄, while Dy³⁺ ions replacing cobalt lattice site, caused magnetic parameters change compared to the pure Co₃O₄ and the hysteresis loop was not observed in doped sample. Finally, we studied the effect of dysprosium additive on charge transfer resistance and oxygen evolution reactions. The results indicated that dysprosium increased the Co₃O₄ conductivity and its catalytic activity towards OER.

ACKNOWLEDGEMENTS

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Table 2. Remanent magnetization (Mr), saturation magnetization (Ms) and coercive force (Hc) for Co₃₋ₓDyₓO₄ in x = 0.0 and 0.04 of Dy³⁺.

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<th>X (molar ratio)</th>
<th>Hc(G)</th>
<th>Hc(G)</th>
<th>Mr(emu/g)</th>
<th>Mr(emu/g)</th>
<th>Ms(emu/g)</th>
<th>Ms(emu/g)</th>
<th>Average particle size (nm)</th>
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<td>0.0</td>
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<td>537.83</td>
<td>20.73</td>
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<tr>
<td>2.5</td>
<td>46.51</td>
<td>348.55</td>
<td>12.78</td>
<td>1.89</td>
<td>0.6493</td>
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<td>36.89</td>
</tr>
</tbody>
</table>

Fig. 17. CV curves for (a) Co₃O₄/GCE, and (b) Co₁.₉₆Dy₀.₀₄O₄/GCE in 0.1 mol L⁻¹ KOH with a sweep rate of 0.05 Vs⁻¹.
CONFLICT OF INTEREST
The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES