Micro/nanostructured MTMOs as Electrocatalysts for Oxygen Evolution Reaction in Alkaline Medium

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Abstract. Different nanostructured mixed transition-metal oxides were synthesized using a facile and controllable hydrothermal method. Incorporation of Cu$^{2+}$ and Ni$^{2+}$ in Co$_3$O$_4$ structure led to an interesting morphological transformation, from quasi-spherical nanoparticles to microspherical urchin-like aggregates of radially assembled nanoneedles. These oxides have notable low crystallite size, narrow size distribution, and high degree of crystallinity. In general, partial cobalt substitution resulted in an improved electrocatalytic activity for oxygen evolution reaction (OER), with NiCo$_2$O$_4$ demonstrating superior performance among the catalysts prepared. It recorded a low overpotential of 374 mV and achieved high stability, making it competitive with state-of-the-art RuO$_2$ and IrO$_2$ (387 mV). This material is of great potential for sustainable energy applications.

1. Introduction

Noble metal oxides, such as ruthenium and iridium oxide (IrO$_2$ and RuO$_2$), remain to be the key electrocatalysts for oxygen evolution reaction (OER) owing to their remarkable electrochemical properties [1]. However, these materials are known to be expensive, nonnaturally occurring, and unstable in alkaline conditions. These impede their use for large scale commercial applications. Such limitations have attracted interest in cheaper and abundant transition metal oxides as new electrocatalysts. In particular, cobaltosic oxide (Co$_3$O$_4$) has attracted huge interest predominantly due to its due to its high redox activity and enhanced stability [2]. The excellent electrochemical stability is attributed to the ease in which cobalt (Co) ion can shift between oxidation states. Furthermore, it has been shown that partial Co substitution by other transition metals (M = Mn, Ni, Cu, Fe, Zn) producing MCo$_2$O$_4$ reduced the cost and toxicity while enhancing the electrochemical performance, through the synergistic effect of individual components [3]. Therefore, various Co-based mixed transition metal oxides (MTMOs) have been synthesized through different techniques such as solvothermal method, thermal decomposition, solution combustion, coprecipitation, and sol-gel process [4-7]. However, these synthesis routes typically require expensive equipment and aggressive experimental conditions. Most of the fabricated Co-based MTMOs of diverse morphologies were also studied for supercapacitor applications only. There also have been no reports about the effects of incorporating transition metal ions in Co$_3$O$_4$ on the resulting morphology of the MTMOs.

In this work, different cobalt-based MTMO nanostructures were fabricated using a facile two-step ethanol-assisted hydrothermal method. Effects on the morphology, structure, electrochemical performance, and stability of the electrocatalysts upon partial Co substitution of Ni$^{2+}$ and Cu$^{2+}$ in
Co$_3$O$_4$ were investigated. Further, the electrolyte concentration was varied to determine its effect on the electrocatalytic behavior of the prepared electrodes.

2. Experimental process
A mixture of 2.0 g urea (NH$_2$CONH$_2$, Techno Pharmchem Haryana) and 0.5 g cetyltrimethylammonium bromide (99%, CTAB, Loba Chemie Pvt. Ltd.) in 20 mL deionized water and 10 mL ethanol (CH$_3$CH$_2$OH, Univar) was stirred for 10 min. Four millimoles of cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich) was added to produce Co$_3$O$_4$. This was further mixed with 2 mmol of either copper (II) nitrate hemi(pentahydrate) (Cu(NO$_3$)$_2$·2.5H$_2$O, Sigma-Aldrich) and nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, RTC Laboratory) to produce different cobalt-based MTMOs. The resulting solution was stirred for 30 min and then transferred to a Teflon-lined stainless steel autoclave reactor. Hydrothermal reaction was carried out in a vacuum oven at 100 °C for 10 h. Thereafter, the precipitate was collected and washed several times with deionized water and ethanol (CH$_3$COOH, Univar) through centrifugation, and then dried in an oven at 60 °C for 6 h. The as-synthesized precursors were calcined in air at 400 °C for 6 h with a heating rate of 1 °C/min.

The size and morphology of the synthesized oxides were observed using field emission scanning electron microscope (FESEM, Hitachi SU-8230). The length and diameter of the nanostructures were measured using Image Processing Analysis in Java software (ImageJ). The crystal structure was analyzed through X-ray diffraction (XRD, Shimadzu XRD-7000) using Cu K$_\alpha$ ($\lambda=1.5406$ Å) while the specific surface area was obtained through Brunauer-Emmett-Teller analysis (BET, Quantachrome Instruments).

The electrochemical performance of the samples was examined using a conventional three-electrode system with 1 M potassium hydroxide (KOH, Sigma-Aldrich) electrolyte. The concentration of KOH was varied from 0.01 to 1.0 M to determine its effect on the electrochemical performance of the catalysts. Ag/AgCl (Autolab 6.0726.107) and platinum (Pt) wire were employed as reference and counter electrodes. A piece of carbon paper drop-cast with the catalyst ink [90% catalyst sample, 10% polytetrafluoroethylene (PTFE, Sigma-Aldrich) binder, and a few drops of ethanol] was used as the working electrode. The mass loading of the prepared catalysts was about 1 mg/cm$^2$. Linear sweep voltammetry (LSV) was performed in the potential range of 0 to 1 V at a scan rate of 1 mV/s to avoid capacitive currents during the measurement. The onset and overpotential were calculated at 1 and 10 mA/cm$^2$ current density ($j$), respectively. Furthermore, to assess the stability of the catalyst in OER, cyclic voltammetry (CV) was carried out at a scan rate of 100 mV/s in the range of 0.4 to 0.8 V for 1000 cycles. All potential values were reported against the reversible hydrogen electrode (RHE).

3. Results and discussion
3.1. Morphological analysis
Displayed in Fig. 1 are the FESEM images of the synthesized (a) Co$_3$O$_4$, (b) NiCo$_2$O$_4$, and (c) CuCo$_2$O$_4$ nanostructures. Quasi-spherical nanoparticles with a mean diameter of about 63.03 nm were observed in pure (undoped) Co$_3$O$_4$ as seen in Fig. 1a-b. Partial substitution of transition metal ions resulted to a dramatic change in the morphology of the precipitates. Upon addition of Ni$^{2+}$, microspheres having a mean diameter of about 3.21 µm were formed. Higher magnification images revealed that the microspheres are actually composed of radially assembled nanoneedles with a mean cross-sectional diameter of 20.62 nm. Particles are also observed to lay on top of the urchin-like structures as seen in Fig. 1d. On the other hand, similar urchin-like precipitates (mean diameter of about 5.75 µm) were obtained when Cu$^{2+}$ was added instead of Ni$^{2+}$. However, the nanoneedles appeared finer with a cross-sectional diameter of about 25.36 nm. This drastic evolution in morphology upon incorporation of transition metal ions could be attributed to a two-stage process.

First, reaction among the precursors yielded nanoparticles that have successively agglomerated to produce large microspheres through oriented attachment [8-9]. It is known that minute nanoparticles have a strong tendency to agglomerate, to minimize their surface energies [8]. Subsequently, incorporation of transition metal ions could provide favorable sites (low interfacial energy) for the absorption of the reactant molecules and direct the anisotropic growth [10,11] which possibly caused
the formation of nanourchins. Furthermore, the formation of micro/nanosized structure could be attributed to the combined effect of ethanol and CTAB during synthesis. Ethanol, when mixed with water, produces an organic solution of low permittivity [12]. This allows the product to be liberated from foreign anions or other ionic species, thus, providing excellent chemical homogeneity. Consequently, nucleation and growth rate are controlled, leading to small particle size. On the other hand, CTAB reduces the surface energy that hinders the growth of the particles [12,13].

Figure 1. Low and high magnification FESEM images of (a-b) Co$_3$O$_4$, (c-d) NiCo$_2$O$_4$, and (e-f) CuCo$_2$O$_4$ after calcination at 400 °C (left) and the XRD patterns (right).

3.2. Structural analysis

The XRD patterns of the synthesized oxides after calcination at 400 °C are also presented in figure 1. Peaks at 2θ = 18.80, 31.15, 36.71, 38.38, 44.62, 55.52, 59.20, and 65.10° are indexed to 111, 220, 311, 222, 400, 422, 511, and 440 planes of Co$_3$O$_4$ (JCPDS Card No. 001-6025), respectively, confirming the formation of pure Co$_3$O$_4$. Interestingly, these peaks are also observed in the diffraction patterns of NiCo$_2$O$_4$ (JCPDS Card No. 001-6025) and CuCo$_2$O$_4$ (JCPDS No. 78–2177). No other peaks, except NiCo$_2$O$_4$, were observed in the sample with Ni, which indicates high purity. After doping with Ni$^{2+}$, the lattice parameter increased from 8.1001±0.0002 to 8.1168 ± 0.0002 relative to pure Co$_3$O$_4$ as shown in Table 1. This suggests the successful incorporation of Ni$^{2+}$ in Co$_3$O$_4$ without altering the spinel structure. In the case of the sample with Cu$^{2+}$, a slight increase in lattice parameter was also observed. Peaks at 2θ = 35.61, 38.83, 48.85, 61.65, 66.62, and 68.20° were indexed to the -111, 111, -202, -113, 022, and 220 planes, respectively, of the monoclinic CuO (JCPDS No. 001-6025). This implies formation of a secondary phase possibly due to the oversaturation of the solid solution of Co and Cu ions, hence producing a CuCo$_2$O$_4$/CuO composite [9,13].

Additionally, it could be observed that the diffraction peaks become relatively wider after the incorporation of metal ions. This could be ascribed to the lower degree of crystallinity or the small crystallite size of the oxides [13], which ranges from about 12.25 to 20.43 nm. Consequently, higher BET specific surface area was recorded with the sample having smaller crystallite size. As shown in Table 1, the 30.83 m$^2$/g specific surface area of Co$_3$O$_4$ becomes 31.72 and 49.04 m$^2$/g, a rise of about 2.8 and 37.1 % upon introducing Cu$^{2+}$ and Ni$^{2+}$, respectively.

Table 1. Crystallite size, lattice parameter, and BET specific surface area of the synthesized oxides.

| Sample       | Crystallite size (nm) | Lattice parameter (Å) | Specific surface area (m$^2$/g) |
|--------------|-----------------------|-----------------------|---------------------------------|
| Co$_3$O$_4$  | 20.43                 | 8.1001 ± 0.0002       | 30.83                           |
| CuCo$_2$O$_4$/CuO | 15.17               | 8.1066 ± 0.0058       | 31.72                           |
| NiCo$_2$O$_4$ | 12.25                 | 8.1168 ± 0.0002       | 49.04                           |
3.3. Electrochemical performance

Shown in figure 2a are the LSV polarization curves of the electrocatalysts for OER. Based on the results summarized in Table 2, CoO₄ obtained an onset potential of 1.57 V vs RHE while CuCo₂O₄/CuO and NiCo₂O₄ both recorded about 1.52 V vs RHE. Overpotential of the catalysts obeys a similar trend, with CoO₄, CuCo₂O₄/CuO, and NiCo₂O₄ registering about 468, 386, and 374 mV, respectively. These partially substituted transition metal oxides perform better than the commercially available RuO₂ (387 mV) and IrO₂ (387 mV) [14] in terms of overpotential. Furthermore, the current density attained at 1.75 V follows the order: NiCo₂O₄ (38.12 mA/cm²) > CuCo₂O₄ (37.67 mA/cm²) > CoO₄ (15.74 mA/cm²). Same trend was observed for mass activity, with values ranging from about 7.01 to 17.84 A/g. This enhancement in electrocatalytic activity upon incorporation of other transition metal ions could be ascribed to the altered Co distribution and introduced vacancies [1] in the CoO₄ structure. Consequently, this leads to an increase in conductivity. In particular, NiCo₂O₄ demonstrated the most excellent electrocatalytic behavior possibly because of its very small crystallite size and high BET specific surface area. Aside from that, its porous nanourchin structure probably provides huge channels that allow effective penetration of the electrolyte, to facilitate the transport electrons during OER. On the other hand, the presence of CuO in CuCo₂O₄/CuO composite could have a detrimental effect in its electrocatalytic property since CuO is highly resistive [9,13].

Further evaluation of the electrocatalytic behavior of each catalyst was conducted by estimating the Tafel slope from the corresponding LSV polarization curves. As presented in figure 2b, CoO₄, CuCo₂O₄/CuO, and NiCo₂O₄ achieved 95.1, 85.0, and 68.4 mV/decade, respectively. These values are relatively low for Co-based systems [9]. This finding supports that NiCo₂O₄, having the best OER kinetics, is the most efficient among the prepared catalysts. Its Tafel slope of about 68.4 is close to 60 mV/decade. This could signify that the rate determining step for water oxidation entails one electron transfer [1,9]. Moreover, this suggests that the most probable functional species in the electrocatalysis of OER is Co³⁺ [14]. Co³⁺ ions are situated in the more exposed octahedral sites of the spinel structure, hence facilitating their oxidation to Co⁴⁺. In addition, presence of such high valent Co cations with a greater number of unpaired d electrons, could lower the activation energy for the chemisorption of gas to the surface of the catalyst. Therefore, both the formation of hydroperoxy species (OOH) and OER are hastened [15], as suggested in equation (3) and (4). The mechanism for OER [15,16] is shown below:

\[
M + OH \rightarrow M \quad OH + e^{-} \quad (1)
\]
\[
M \quad OH + OH \rightarrow M \quad O + H_{2}O + e^{-} \quad (2)
\]
\[
M \quad O + OH \rightarrow M \quad OOH + e^{-} \quad (3)
\]
\[
M \quad OOH + OH \rightarrow M \quad O_{2} + H_{2}O + e^{-} \quad (4)
\]

where M is the active species. Meanwhile, based on this series of reactions, decreasing the amount of OH⁻ would inhibit the formation of O₂. This is clearly shown in figure 2d, wherein a dramatic reduction of current density (38.12 to 0.03 mA/cm²) and an apparent shift to higher onset potentials were observed after lowering the KOH concentration from 1 to 0.01 M. On the other hand, stability is an equally important measure of a good electrocatalyst, especially for upscale applications in energy storage and conversion systems. As illustrated in figure 2c, all the catalysts showed good stability even after 1000 cycles, recording a quite minimal 4.13 to 4.88 % drop in current density at 1.75 mV.

**Table 2.** Summary of the electrocatalytic activity of the MTMOs in 1 M KOH.

| Sample     | Overpotential (mV) | Tafel slope (mV/dec) | j at 1.75 V (mA/cm²) | Mass activity (A/g) |
|------------|--------------------|----------------------|---------------------|---------------------|
| CoO₄       | 468                | 95.1                 | 15.74               | 7.01                |
| CuCo₂O₄/CuO| 386                | 85.0                 | 37.13               | 11.12               |
| NiCo₂O₄   | 374                | 68.4                 | 38.12               | 17.84               |
4. Conclusion

Different nanostructured cobalt-based MTMOs were fabricated using a facile two-step hydrothermal method. Initially, Co$_3$O$_4$ quasi-spherical nanoparticles were formed. Addition of Cu$^{2+}$ and Ni$^{2+}$ resulted to the formation of microspherical urchin-like aggregates of radially assembled nanoneedles. This dramatic morphological transformation could be accounted for the incorporation of metal ions in the Co$_3$O$_4$ structure. Remarkably, the nanostructures have regular shapes, micro/nanosized crystals, and high degree of crystallinity, which are possibly imparted by the introduction of ethanol and CTAB during synthesis. In general, partial cobalt substitution with other transition metal ions led to an enhanced electrochemical performance, with NiCo$_2$O$_4$ exhibiting superior activity. This material is of great potential for energy storage.

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