# THREE-DIMENSIONAL YARN BALL-LIKE NICKEL COBALT OXIDE AS AN ELECTROCATALYST MATERIAL FOR FUEL CELL APPLICATION

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**Abstract**. The shape, size and specific surface area play a major contribution in determining the catalytic activity of an electrocatalyst. In order to control them, hydrothermal reaction time is one of important parameter tailoring the desired morphological and structures. Through this facile method, nickel cobalt oxide ($NiCo_2O_4$) has been successfully synthesized with various reaction time (6, 12, 18, 24h). The cubic spinel crystal of all the synthesized $NiCo_2O_4$ is obtained according to the standard pattern. The smallest crystallites size of 19.12 nm is obtained by powder synthesized for 18 hours based on the Scherrer formula calculation from X-ray diffraction (XRD) analysis. The field emission scanning electron microscopy (FESEM) micrograph demonstrates all the synthesized $NiCo_2O_4$ consists of three-dimensional (3D) nanoflakes that interconnected to each other and resemble a yarn ball with deteriorated structures when the reaction time is increasing. From Brunauer–Emmett–Teller (BET) analysis, the 3D yarn ball-like structures synthesized for 6 hours yield a very high specific surface area. The ultrathin nanoflakes provide a large surface area to accelerate the electrochemical reaction of the catalyst thus increase the performance of a fuel cell system. Hence, this 3D yarn ball-like $NiCo_2O_4$ synthesized by hydrothermal can be a promising electrocatalyst material for fuel cell application.

**Keywords:** Nickel cobalt oxide, binary transition metal oxide, specific surface area, 3D nanostructures, fuel cell

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## Introduction

The dominos effect of an increase in global population that leads to a rise in energy demand and environmental issues have become a major concern, especially in a developing country [1]. At this moment, the over-reliance on non-renewable energy sources such as fossil fuels leads to quicker depletion of the resources and soar environmental pollution [2]. In order to tackle these alarming issues, there is a need to explore a new clean, affordable and efficient energy conversion and generation system. Fuel cell is a high efficiency electrochemical device which convert chemical energy directly to electrical energy and does not emit any greenhouses gases into the environment [3]. Owing to these advantages, fuel cell technology has shifted the current interest into the exploration of the current, green and high efficiency power generation system.

Fuel cell is made up of basic components such as anode, cathode and electrolyte. On top of that, there is electrocatalyst needed on both anode and cathode sides to speed up the anodic oxidation and cathodic reduction reaction respectively. As one of the key parts of fuel cell system, this electrocatalyst must possess certain criteria such as having a high catalytic activity to ensure the excellent performance of fuel cell [4-5]. In recent days, noble metals such as platinum (Pt), gold (Au) and palladium (Pd) have been commonly employed as electrocatalysts as they possess the criteria mentioned. However, in terms of stability after a long run and operation, these types of metals tend to degrade due to interface corrosion between the catalyst and electrode. What makes it worst, the price for these noble metals are very expensive, thus, hindering their practical, large-scale application and commercialization [6].

Considering these advantages, on-going research are leaning to explore high performance and cost-effectiveness of non-precious metals for electrocatalyst. Recently, a bimetallic oxide $NiCo_2O_4$ is considered one of the promising electrocatalyst for oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) as its conductivity is about two orders of magnitude higher than those single metal oxides (NiO and $Co_3O_4$) [7]. High conductivity leads to better electrochemical performance as more electrons are transferred during the reaction.

Apart from the remarkable properties possessed by the materials, their morphologies also give an impact towards the electrochemical properties. Three dimensional (3D) $NiCo_2O_4$ such as, urchin-like [8], flower-like [9] and nano-flakes [10] have advantages in terms of large specific surface area which can improve electrolyte permeability and ion transfer. In order to produce the 3D nanostructures, template method is used. However, adding a template will increase the cost of materials preparation. $NiCo_2O_4$ prepared by the sol-gel method in other way tends to agglomerate and also hinder by high cost.

Presently, a hydrothermal method is widely employed to synthesize controllable morphology of nanostructures under certain temperatures, pressure, and reaction times. These parameters are crucial in determining the feasibility for the $NiCo_2O_4$ being produced in mass production. The reduction of either parameter contributes to lowering the cost of production.

Therefore, in this study, we reported the synthesizing of 3D yarn-ball like nanostructures of $NiCo_2O_4$ through facile hydrothermal method prepared at different reaction times. The synthesized $NiCo_2O_4$ with the shortest reaction time exhibited the highest specific surface area indicating great potential as high performance electrocatalyst for fuel cell application.

## Materials and Methods

All precursors and solvent which are cobalt nitrate hexahydrate [$Co(NO_3)_2$•$6H_2O$], nickel nitrate hexahydrate [$Ni(NO_3)_2$•$6H_2O$] and 1-methyl-2-pyrrolidinone (NMP) were purchased from Sigma-Aldrich. These materials in this experiment were used as received without further treatment.

### *Synthesis of $NiCo_2O_4$*

Typically, two precursors, cobalt nitrate hexahydrate 1 mmol [$Co(NO_3)_2$•$6H_2O$] and 1 mmol nickel nitrate hexahydrate were dissolved in organic solvent, NMP and water, $H_2O$ with volume ratio 1:1. The mixture was stirred up to half an hour or until all the solid was dissolved completely. Then, the mixture was transferred into a sealed 100 ml Teflon-lined autoclave (the process known as hydrothermal) and heated at 180 °C for 6, 12, 28 and 24 hours. After it was cooled at room temperature, the solution was centrifuged to collect the dark green precipitate. Afterwards, the precipitate was washed with deionized water and ethanol before dried. Lastly, the dried powder was collected and calcined under argon atmosphere at 300 °C for 6 hours. Based on different reaction time, the samples are named as $NiCo_2O_4$-6, $NiCo_2O_4$-12, $NiCo_2O_4$-18 and $NiCo_2O_4$-24

### *Characterization of $NiCo_2O_4$*

The crystallographic structures and morphologies of the samples were analyzed and observed using X-ray diffraction (XRD) (Brand: Bruker; Model: D8 Advance) and field emission scanning electron microscope (FESEM) (Brand: Zeiss; Model: Supra 55VP) respectively. The Brunauer-Emmett-Teller (BET) measurements were employed to estimate the surface area of samples (Brand: Micromeritic; Model ASAP 2020).

## Results and Discussion

### *XRD Characterization*

Based on XRD patterns of $NiCo_2O_4$ samples that can be observed in Figure 1, all the diffraction peaks appeared to be matched with the standard pattern of $NiCo_2O_4$ (JCPDS No 20-0781) [11]. The peaks were corresponding to (220), (311), (400) and (440) crystal planes of $NiCo_2O_4$. The Debye-Scherrer formula as follow was used to calculate the $NiCo_2O_4$ crystal plane sizes:

$$d_{XRD} = 0.9\lambda/(\beta_{\frac{1}{2}} cos\theta) \quad (1)$$

where $d_{XRD}$ is the crystal plane sizes, $\lambda$ is the incident X-ray wavelength and $\beta_{1/2}$ is the full width at a half maximum, $\theta$ is the angle at the peak maximum. It illustrated the porous nanostructures of the materials and size of $NiCo_2O_4$ crystallites possessed by $NiCo_2O_4$-6, $NiCo_2O_4$-12, $NiCo_2O_4$-18 and $NiCo_2O_4$-24 can be calculated by the Scherrer formula (equation 1), based on the strongest peaks ($2\theta = 43.65°$). The lattice parameter was calculated from the d-(4 0 0) and the results was summarized in Table 1. This value was not far from the reported value (0.808 nm) [12]. It was clear that the particles that were in nano-sized range had larger active area which later will be confirmed by BET analysis.

**Table 1:** Crystallites sizes, d-spacing and lattice parameter for each synthesized sample

| Samples | Crystallites size (nm) | d-spacing (Å) | Lattice parameter (nm) |
|---|---|---|---|
| $NiCo_2O_4$-6 | 21.11 | 2.08 | 0.8332 |
| $NiCo_2O_4$-12 | 20.60 | 2.07 | 0.8288 |
| $NiCo_2O_4$-18 | 18.30 | 2.06 | 0.8253 |
| $NiCo_2O_4$-24 | 20.50 | 2.08 | 0.8323 |

A peak shift to lower angles was detected between 35° to 39° on plane (3 1 1) when the reaction time was increased. This phenomenon was due to structural defects (i.e oxygen vacancies) formed. Hence, increasing the reaction time brings a major impact to the structural morphology. Lattice expansion due to the relaxed metal-oxygen bonds and higher ionic radius brought on by the absence of oxygen causes a minor XRD peak shift to lower angles [3,6,10].

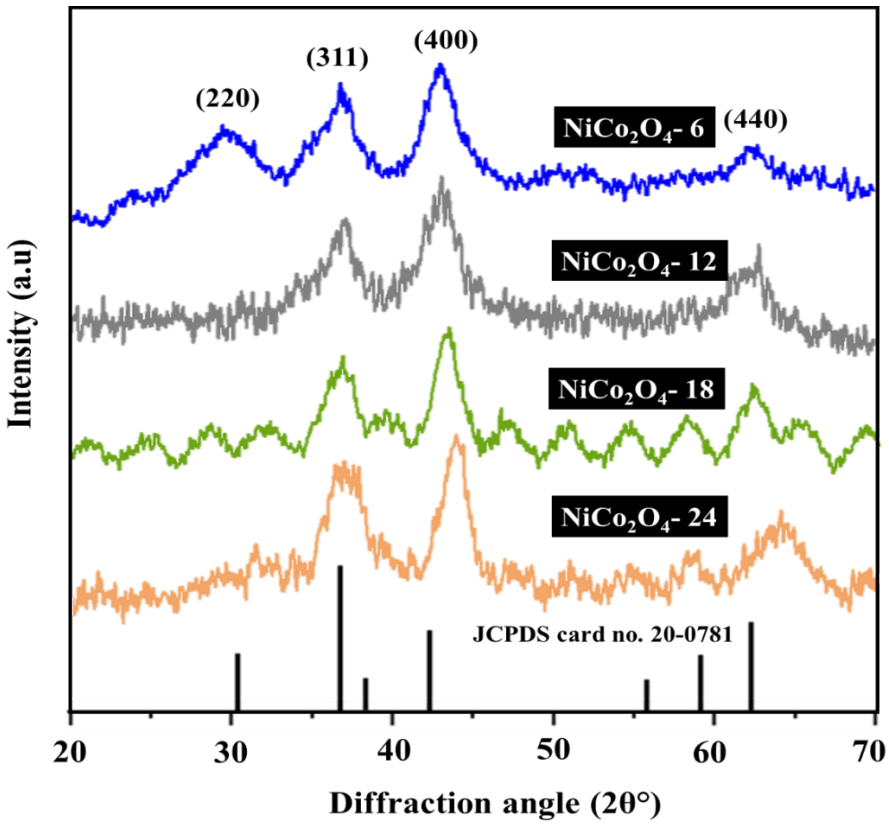


**Figure 1:** XRD patterns of the synthesized powder $NiCo_2O_4$ with various reaction time

### *FESEM Characterization*

Thin nanoflakes that interconnected to each other made up hierarchical structures were displayed by all samples. The yarn-ball like nanostructures occurs via a mechanism that involves recrystallization and nucleation after varied reaction time. The mechanism of $NiCo_2O_4$ synthesis is illustrated in Figure 2.

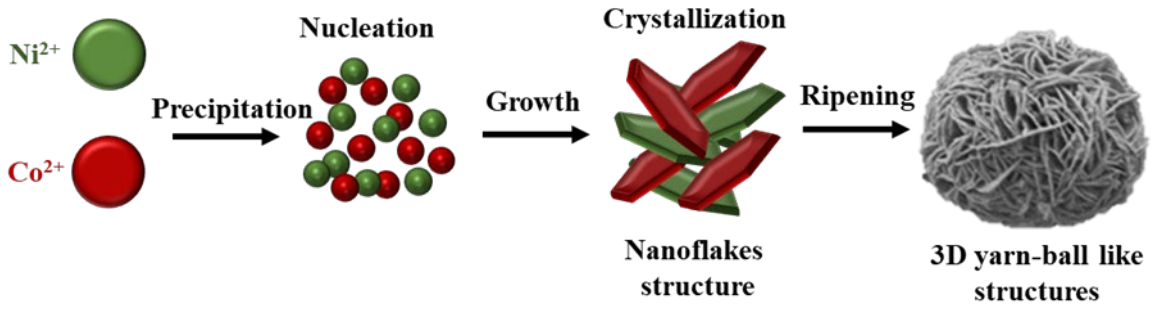


**Figure 2:** The yarn ball-like $NiCo_2O_4$ synthesis mechanism is depicted schematically.

The surface morphology and microstructures of the $NiCo_2O_4$ was observed by FESEM. Figure 3 show the morphologies of $NiCo_2O_4$-6, $NiCo_2O_4$-12, $NiCo_2O_4$-18 and $NiCo_2O_4$-24.

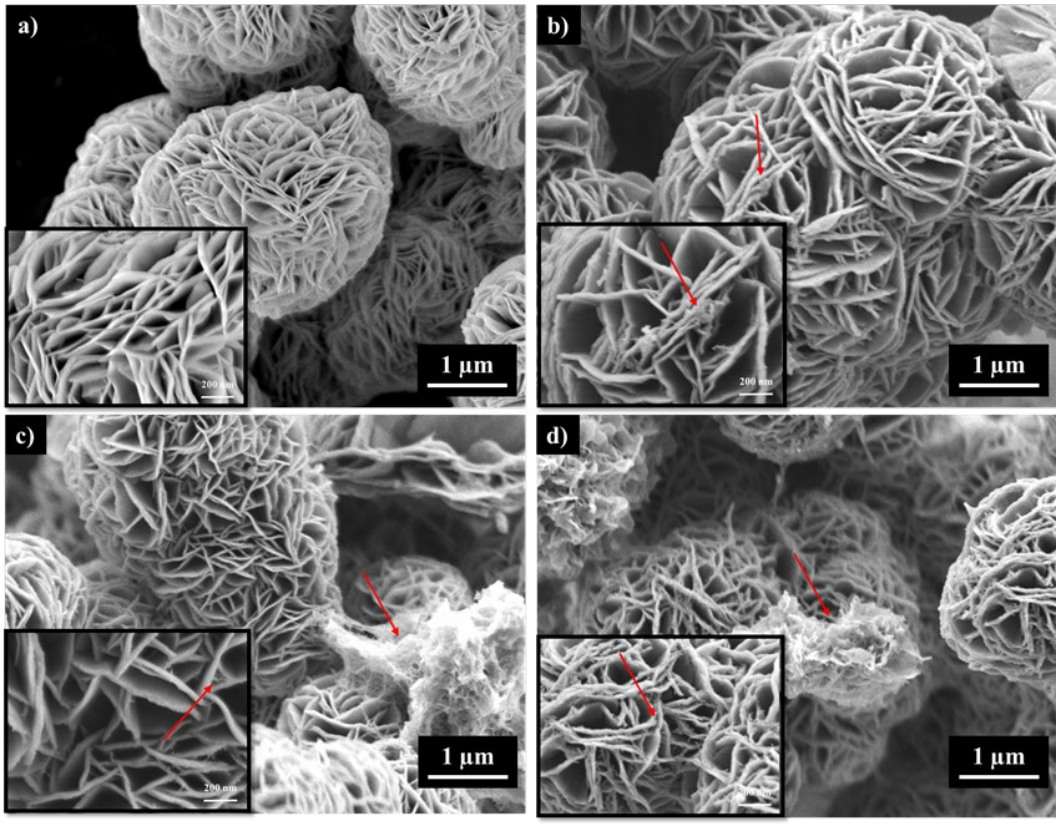


**Figure 3:** FESEM micrographs of $NiCo_2O_4$ produced at various reaction time (a) 6 hours, (b) 12 hours, (c) 18 hours and (d) 24 hours. Inserts showed images at different magnification. Red arrows pointed the degradation.

As they thin nanoflakes were formed loosely, there were nano-void between them that form mesopores structures. Sample $NiCo_2O_4$-6 (Figure 3(a)) demonstrated 3D yarn ball-like nanoflakes structure with smooth and highly uniform porosity. It was believed that the mesoporous 3D yarn ball-like structures of nanomaterials can provide larger specific surface area and improved pore properties. These properties can greatly increase the electrochemical performances. On the other hand, when the reaction time was increased to 12, 18 and 24 hours (Figures 3(b) to (d)), the nanoflakes structures started to degrade indicating the decomposition of the nickel-cobalt layered double hydroxide (pointed by red arrow in Figure 3). These degradation will affect the pore properties and limit the electron/ion transfer through it. Hence, reduce the electro-catalytic reactivity [14].

### *$N_2$ Adsorption-Desorption Characterization*

The $N_2$ adsorption-desorption characterization was employed to further clarify the porous nanostructure of the sample. As is well known to us, the specific surface area, pore diameter and volume are important factors influencing the electro-catalytic performance of the materials [15]. Figure 4 showed the nitrogen adsorption-desorption isotherms of the temperature-dependent synthesized-$NiCo_2O_4$. As can be seen the figures, all the isotherms were in similar form and increased steadily in medium relative pressure region to higher pressure. This may attributed to condensation of capillary and illustrated the existence of nanoporous structures in the samples. The steep curves in the high pressure region may be due to adsorption in the pores among the nanoflakes [10].

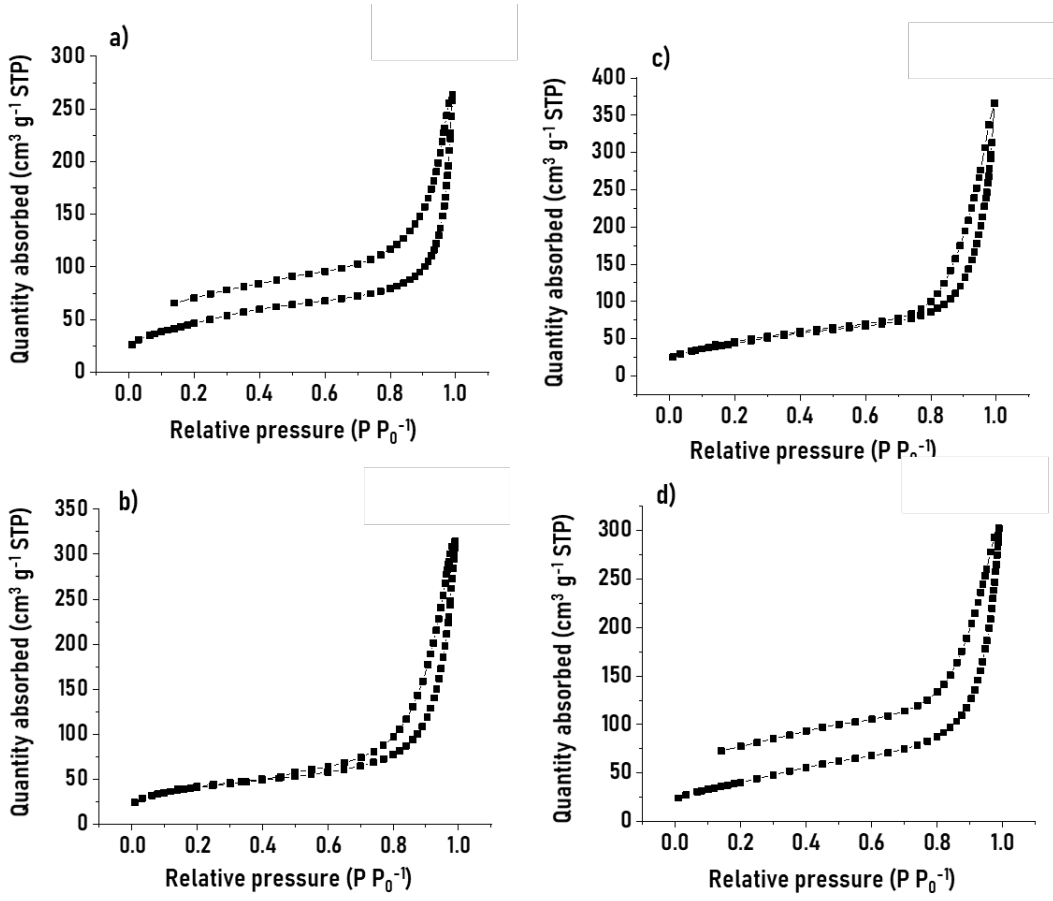


**Figure 4:** $N_2$ adsorption and desorption isotherms of (a) $NiCo_2O_4$-6, (b) $NiCo_2O_4$-12, (c) $NiCo_2O_4$-18 and (d) $NiCo_2O_4$-24

The highest specific surface area was 169.61 $m^2g^{-1}$ obtained by $NiCo_2O_4$-6. The number of exposed active sites could greatly rise due to the increased specific surface area. As a result, improved electrocatalytic performance is expected. The wide pore distribution can effectively create a triple phase boundary site and enable effective mass and electron transport throughout the catalytic process. However, varying the reaction time, the pore diameter and pore volume of the $NiCo_2O_4$ was not showing distinct values. Alas, the specific surface area for all samples showed outstanding and comparable values compared to previous studies [4,16-17]. Table 2 shows the specific surface area, average pore diameter and total pore volume of all samples.

**Table 2:** Structural parameters gained from BET analysis

| Reaction time (hours) | Specific surface area ($m^2$ $g^{-1}$) | Average pore diameter (nm) | Total pore volume ($cm^3$ $g^{-1}$) |
|---|---|---|---|
| 6 | 169.61 | 38.41 | 0.40 |
| 12 | 140.13 | 41.36 | 0.48 |
| 18 | 160.71 | 33.35 | 0.58 |
| 24 | 152.26 | 38.22 | 0.48 |

## Conclusions

In summary, $NiCo_2O_4$ with a hierarchical 3D yarn ball-like porous nanostructures were successfully synthesized using a facile hydrothermal method in reduced time. This shorter reaction time will contribute to lower manufacturing cost hence will open up the opportunity for commercialization and larger scale production. The hierarchical 3D nanostructured $NiCo_2O_4$ build-up from interconnected thin nanoflakes with uniform structures has proven to yield a high specific surface area, adequate pore size and volume. These criteria play major role in electrochemical performance of energy storage application due to rapid transmission of electrolyte ions inside the cell. Finally, the hydrothermal parameter in this study brings a major enhancement on the morphology and structural properties of $NiCo_2O_4$ which could be a great potential to be applied in fuel cell application.

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## Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

## Disclosure of conflict of interest

The authors have no disclosures to declare.

## Compliance with ethical standards

The work is compliant with ethical standards.

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