



# Simple room temperature synthesis of porous nickel phosphate foams for electrocatalytic ethanol oxidation

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## ABSTRACT

The simple and eco-friendly fabrication of non-noble metal catalyst is of great importance for sustainable energy production from alcohol. Herein, we report the new synthetic route for the preparation of nickel phosphate nanostructure through simple co-precipitation method. We studied the effect of annealing temperature ranging from 500 °C to 1100 °C on the electrocatalyst for ethanol electro-oxidation. In addition, we demonstrate that the resulting nickel phosphate materials can serve as efficient transition metal electrocatalyst for the ethanol oxidation under alkaline condition. In particular, the nickel phosphate annealed at 900 °C (NP-900) affords higher current density of 1.2 mA cm<sup>-2</sup> at the low potential of 0.7 mV, demonstrating great catalytic stability as well as good cyclability for 1000 cycles giving about 92% faradaic yield towards the ethanol.

## 1. Introduction

The development of highly efficient and clean energy sources has become an important and urgent requirement due to the energy crisis, air pollution and global warming issues. Varieties of fuel sources such as natural gases, bio-wastes, hydrogen, methanol, ethanol, hydrocarbons (especially the smaller organic molecules) etc. are being used for this purpose [1,2]. Among various energy production system, the acid-alkaline hybrid fuel cell has been considered as one of the most promising choices due to its excellent energy conversion ability, convenience in handling, average operating temperature range and also the alcohols possess higher energy density compared to other sources [1,3]. Further, the fuel gets electrochemically oxidized at the anode cleanly without producing any harmful pollutants [4,5].

So far, noble-metal based catalyst including Pt-Sn [6], carbon supported Pt/NiO [7], ternary composite of Pt, Sn, Ce and C [8], Pt nanostructures [9], bimetallic Pd-Ag composite [10], Au-Pt nanodendrites [11], AuNP/PPy/rGO composites [12] etc. have been extensively explored for fuel cell and sensor applications. However, being expensive and the poisoning of the catalyst limit its use to the real world applications. Hence, the researchers have been deeply exploring an alternative non-noble metal based catalyst especially transition metals (including metal oxides, sulfides etc.) in recent years. Among various

transition metal oxides/sulfides, nickel based materials were extensively used for fuel cell applications such as nickel phosphate nanoparticles [5], nanocomposite of NiCo<sub>2</sub>O<sub>4</sub>-MWCNT aerogel [13], N-doped activated C along with Ni nanorods [14], polycrystalline nickel foil [15], nickel phosphate along with MWCNT [16], nickel nanoparticle along with commercially available Vulcan XC-72R carbon [17] and nitrogen doped rGO supported with Ni-Co nanoparticles [18] etc.

Recently, metal phosphates are largely focused on many potential applications due to its unique physical and chemical properties and simple synthesis procedure [19–24]. The transition metal phosphate is not much explored in fuel cell applications. In particular, nickel phosphate material is very attractive in fuel cell application because of its excellent redox electrochemical property. Currently, few reports are available in supercapacitor applications using this nickel phosphate material [20–23,24]. Hence, the fabrication of nickel phosphate nanostructure with improved electro-catalytic properties is highly desirable for fuel cell applications.

In this present work, we report an eco-friendly (without the aid of a surfactant and organic solvent) and scalable method (easy chemical precipitation route) for the synthesis of nickel phosphate nanostructure. The as-prepared nickel phosphate exhibited an excellent electro-catalytic behaviour for electro-oxidation of ethanol.

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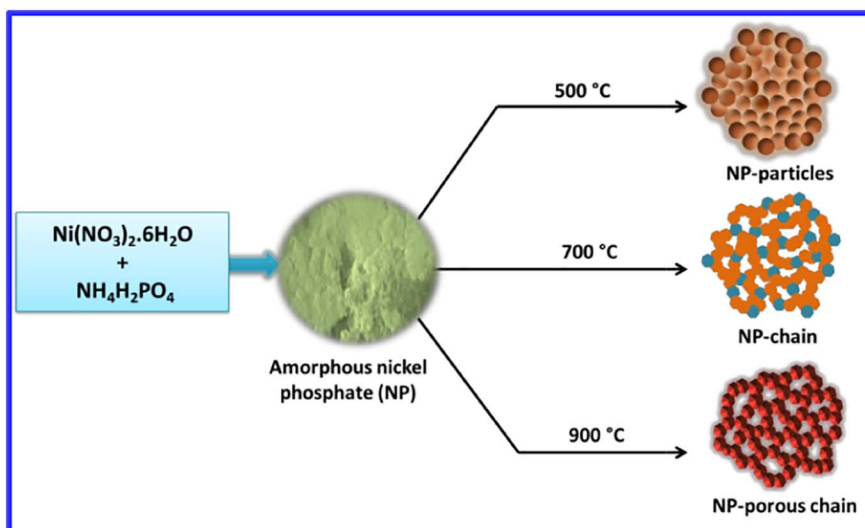
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**Scheme 1.** Schematic illustration of the phase transformation at different annealing temperature.

## 2. Experimental

### 2.1. Materials and reagents

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and Nafion (5 wt%) were purchased from Sigma Aldrich. Ethanol, isopropanol and sodium hydroxide were obtained from Daejung chemicals Ltd., South Korea. All the reagents were of analytical grade and hence used without further purification. All the aqueous solutions required for experimental purpose were prepared with deionized (DI) water (18.2  $\text{M}\Omega\text{-cm}$ , Elga DI water system).

### 2.2. Apparatus and measurements

The phase identification and the crystalline nature of as-prepared material were analyzed with the aid of powder X-ray diffraction technique (XRD) (Rigaku, operating at 40 keV/40 mA). The surface morphology was clearly characterized using a field emission-scanning electron microscopy (JEOL JSM-5900) along with energy dispersive X-ray (EDX) system and high resolution transmission electron microscopy (HR-TEM, JEOL JEM-2010). The electrochemical experiments were analyzed using a Versastat 4 electrochemical workstation. A conventional three-electrode system which comprised of modified glassy carbon electrode (GC having a diameter of 3 mm) as the working electrode, Pt wire as a counter electrode and Ag/AgCl (3 M KCl) as the reference electrode were used for the electrochemical measurements such as cyclic voltammograms (CV), double step chronoamperograms (CA) at room temperature. NaOH (0.5 M) was chosen as an electrolyte solution and the entire electrochemical measurements were performed in it.

### 2.3. Preparation of nickel phosphate

4.0 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1.5 g of  $\text{NH}_4\text{H}_2\text{PO}_4$  were taken and dissolved completely in distilled water under constant magnetic stirring. To the above solution, 0.5 M KOH solution was added gradually in a drop-wise manner which acted as a precipitating agent. Here,  $\text{NH}_4^+$  ion involves for the complex formation of ammonium nickel phosphate (Eq. (3)). The detailed mechanism for the formation of ammonium nickel phosphate has been given below (Eqs. (1) to (3)).



It was then allowed to stir for around 120 min. Then, the resulting

precipitate was collected. It was then washed repeatedly with distilled water and then dried in a vacuum oven overnight maintained at 60 °C. Further the obtained powder was annealed at three different temperatures 500 °C, 700 °C and 900 °C in a muffle furnace at the heating rate of 2.5 °C  $\text{min}^{-1}$  for 4 h to improve the crystalline nature of the product and eliminate the water molecules (Scheme 1). The prepared nickel phosphate at 500 °C, 700 °C and 900 °C were designated as NP-500, NP-700 and NP-900, respectively.

### 2.4. Electrode preparation and modification for ethanol electro-oxidation

The nickel phosphate modified electrode was prepared following the below protocol. In the first step, the bare glassy carbon (GC) electrode was mechanically polished with alumina suspension (0.5 and 1.0  $\mu\text{m}$ ) on micro polishing kit and rinsed with ethanol which was followed by ultra-sonication to remove the alumina residues. In the second steps, a 10  $\mu\text{L}$  aliquot of nickel phosphate (2 mg in 0.18 mL of isopropanol and 20  $\mu\text{L}$  of 5 wt% Nafion solution) was drop-casted over the surface of cleaned GC surface and air-dried at room temperature.

## 3. Results and discussion

### 3.1. Materials characterization

The structure and morphology of the nanostructured nickel phosphate annealed at different temperature (500, 700 and 900 °C), were characterized by field emission electron scanning micrographs (FE-SEM). Fig. 1 shows the FE-SEM micrographs of nickel phosphate calcinated at 500 °C (A), 700 °C (B) and 900 °C (C). The inset shows the images of the corresponding samples with higher magnification. Here, we can clearly observe that the influence and effects of temperature on the morphology and the growth pattern of the particles.

The as-prepared sample without heat treatment which is amorphous in nature shows agglomerated small particles formed as a lump (Fig. S1). NP-500 image visualizes the presence of agglomerated bigger particles with an average particle size of around  $40 \pm 5 \text{ nm}$  (Fig. 1A) when compared to the pristine sample. It clearly suggests that the particle size has started growing at this temperature. Further, when increasing the temperature to 700 °C and 900 °C, we can observe the disappearance of particles-like structure and its transformation to clear porous and inter connected chain-like structure (Fig. 1B and C) with an average size of around  $60 \pm 5 \text{ nm}$  and  $100 \pm 5 \text{ nm}$  respectively. This porous structure is much essential for the improved electro-catalytic applications. The NP-900 sample was further examined by energy dispersive X-ray spectroscopy (EDX) elemental mapping in order to

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