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Reflux-based synthesis and electrocatalytic characteristics of nickel phosphate nanoparticles

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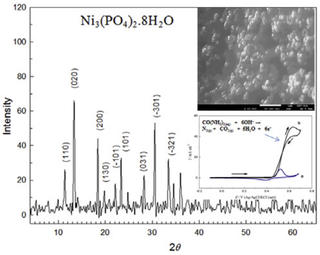
HIGHLIGHTS

- Nickel phosphate (NiPh) nanoparticles were synthesized using reflux-based method.
- XRD pattern and FTIR spectrum suggests $Ni_3(PO_4)_2.8H_2O$ phase.
- It has monoclinic crystallographic form and it was casted on glassy carbon (GC).
- GC/NiPh demonstrates electrocatalytic activity toward urea oxidation in 0.5 M KOH.

GRAPHICAL ABSTRACT



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ABSTRACT

This is a first report on the synthesis of nickel phosphate nanoparticles (N-NiPh) from its precursors using a reflux-based route at 90 °C and its use for destruction and conversion of urea (a biochemical species) to useful fuel (H_2 gas). The prepared particles are characterized by different techniques including: X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR spectroscopy and BET surface area determination. The particle size is found to have an average value of ~70 nm with surface area of 22.3 m^2/g. According to the XRD pattern and FTIR spectrum, the obtained phase structure of the NiPh nanoparticles is $Ni_3(PO_4)_2.8H_2O$ with a monoclinic crystallographic form. Using cyclic voltammetry (CV) (and also EIS), the N-NiPh modified glassy carbon electrode (GC/N-NiPh) is activated upon potential cycling in 0.5 M KOH for 75 cycles. This is obtained at the maximum attainable enrichment of the N-NiPh surface by Ni(II)/Ni(III) species. The GC/N-NiPh shows superior electrocatalytic activity towards urea oxidation from alkaline solution compared to the corresponding $Ni(OH)_2$-based electrodes. The oxidation process is analyzed in the light of the measured and collected electrochemical data.

1. Introduction

Metal phosphates have found great interest both from academic and technological point of view due to its unique chemical and catalytic properties [1–3]. They have been used as biomaterials for tissue engineering applications [4–6], as catalysts for chemical conversion [7,8] and other fields such as drug delivery [9] and antibacterial activity [10,11]. Of these phosphate materials, nickel phosphate represents an important material. It has been used in many applications such as supercapacitors [12,13], lithium batteries [14,15], catalytic reactions [16] and electrocatalytic reactions [17]. Based on the literatures, nickel phosphates are currently prepared

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via different approaches such as wet chemical process [18,19], hydrothermal [20], solvothermal [21,22] and sol-gel technique [23]. Those different approaches led to a variation in the chemical composition, structural and morphological properties which have been the main reasons for the presence of nickel phosphate in several applications. Wu *etal.* [24] reported that different morphologies of nickel phosphate were obtained through controlled synthesis technique via simple template hydrothermal technique.

Synthesis of Nano/micro sizes of nickel phosphate particles using surfactants, ligands or solid membrane templates has been found in literatures [25]. Although the hydrothermal process is a friendly environmental technique and calcination step is not required, it has two major drawbacks. It is costly and time consuming process [26]. Developing a unique synthesis route to obtain similar morphological structures that produced by high temperature hydrothermal process is still a challenging work. Reflux-based method can handle those drawbacks of the hydrothermal method since it is simple process and cost effective. In the present work, obtaining nanoparticles of nickel phosphate is one of the main goals of this study. The impacts of the produced nanostructured of nickel phosphate on the catalytic oxidation of urea, for the first time in literatures, will be assessed here in the present work. To the best of our knowledge, the synthesis of nickel phosphate from its precursor salts via reflux route is not reported.

Searching for new energy sources and prevention of water pollution considered to be a challenge for scientists and engineers worldwide. Conversion of biochemical species (*e.g.*, urea) to useful fuels is a matter of interest from academic and practical point of view [27,28]. In this context, electrocatalytic oxidation of urea has gained a growing attention during the last decade for producing hydrogen. Urea constitutes a major fraction of the human urine and of industrial wastes and hence represents an environmentally problematic issue [29,30]. The literature reported the conversion of industrial waters of high concentrations of urea to pure H_2 gas in basic solutions [29,30]. Biodegradation of those molecules to NO_2^- and NO_3^- may lead to many diseases to human [31]. Electrolysis of urea solution in alkaline solution can be considered as an anodic urea oxidation producing nitrogen and carbon dioxide and H_2 gas at the cathode. The latter with high purity can be considered as a desirable fuel with high purity by-product [32]. Combination with waste water treatment units, the latter electrolysis process can be considered as an economically feasible process when compared with other techniques [32]. It has long been known that Pt-based electrocatalysts are unavoidable candidate for oxidation of organic molecules. However, Ni-based electrocatalysts can represent good substituents for the above electrocatalysts especially for small molecules [33,34]. The above argument calls for research to find new catalysts for such important catalytic process.

Based on the above consideration, the main purpose of the present work is to synthesize nanoparticles of nickel phosphate (N-NiPh) with reflux method and also to using N-NiPh in electrocatalytic oxidation of urea from alkaline solutions. The morphological and structural properties of the N-NiPh will be studied using X-Ray spectroscopy, scanning electron microscope (SEM), FT-IR absorption spectroscopy and BET surface area determination. The electrochemical and electrocatalytic properties of the GC/N-NiPh are studied by cyclic voltammetry (CV) and also by electrochemical impedance spectroscopy (EIS).

2. Experimental

All chemicals used in this work were of analytical grade. They were purchased from Fisher and Sigma-Aldrich and were used as received without further purification. All solutions were prepared using double distilled water.

2.1. Synthesis of nickel phosphate

Nickel phosphate was synthesized using a reflux-based route. A precipitate of nickel phosphate was mainly prepared from nickel nitrate ($Ni(NO_3)_2.6H_2O$) and ammonium dibasic phosphate ($(NH_4)_2HPO_4$). The procedure can be summarized as follows. A 5 ml of 2 M solution of each of nickel nitrate and dibasic ammonium hydrogen phosphate were mixed together at room temperature in a round bottom flask with continuous stirring. Directly after mixing, a greenish precipitate is formed. Few drops of conc. nitric acid were added to dissolve the precipitate and to get a uniform homogenous solution. A 30 ml of 0.8 M urea solution was added to the homogenous mixture. The round flask was connected to a condenser and maintained at a definite refluxing temperature of 90 °C with a uniform gentle stirring for 18 h. After refluxing process, a greenish suspension was obtained which it was left to cool to room temperature, filtered and washed several times with bi-distilled water. Finally, the precipitate was left in an oven at 100 °C to dry for overnight to be ready for different characterizations.

The catalyst ink of nickel phosphate nanoparticles (N-NiPh), for being anchored on the surface of glassy carbon electrode (GCE), was prepared by adding the proper mass of the N-NiPh powder (5 mg) in a test tube containing 2.5 ml isopropanol + 50 μL of Nafion solution (5% in water). The above mixture was sonicated for 30 min in an ice bath.

2.2. Electrode modification

Glassy carbon electrode, GC ($d = 2$ mm) is used here as the underlying substrate for nickel phosphate nanoparticles. It was cleaned by mechanical polishing with aqueous slurries of successively finer alumina powder (down to 0.06 μm), then washed thoroughly with doubly distilled water and then with ethanol. Next, 50 μL of a freshly prepared N-NiPh suspension (prepared as given above) is casted onto the thus cleaned GC electrode and left overnight for drying in air. The prepared loading level is 3.0 mg cm^{-2} (of the electrode surface area).

2.3. Measurements

The phase structure of the synthesized product was studied using X-ray diffraction (XRD). The XRD pattern was obtained using a diffractometer ((PANalytical, X'Pert PRO) equipped with a Cu Ka radiation ($\lambda = 1.5406$ A°). XRD radiation generated at 40 KV and a current of 44 mA with a scan rate of 2°/min over a 2° range of 4-80°. The infrared spectra (FT-IR) was performed by using JASCO 3600 spectrophotometer using ca. 0.5 mm KBr pellets containing 2.5 wt % sample. The surface of the N-NiPh sample was investigated using scanning electronic microscopy (SEM, Model JEOL JSM 5410, Japan).

The BET specific surface area of the samples was examined using low-temperature (77.38 K) nitrogen adsorption isotherms measured over a wide range of relative pressures from 0.02 to 0.9 atm. Adsorption measurements were performed on a Micrometrics ASAP2010 volumetric adsorption apparatus. High-purity nitrogen (99.999%) was used. Prior to measurement, the samples were degassed at 40 °C for 18 h in the degas pot of the adsorption analyzer.

Electrochemical measurements were performed using Gamry potentiostat/galvanostat supported with Gamry electrochemical analysis technique. Electrochemical measurements were carried out in a conventional three-electrode cell. The counter electrode was made of a platinum coil. The reference electrode was Ag/AgCl/KCl (sat.) with a Luggin probe positioned near the electrode surface. The potential throughout the text is referred to the above reference electrode. The EIS measurements were carried out in the frequency