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 Ni3(PO4)2.8H2O 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.

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 (H2 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 m²/g. According to the XRD pattern and FTIR spectrum, the obtained phase structure of the NiPh nanoparticles is Ni3(PO4)2.8H2O 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...
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 et al. [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 H2 gas in basic solutions [29,30]. Biodegradation of those molecules to NO2 and NO3 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 H2 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 substitutes 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(NO3)2.6H2O) and ammonium dibasic phosphate ((NH4)2HPO4). 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 (Ni-NiPh), for being anchored on the surface of glassy carbon electrode (GCE), was prepared by adding the proper mass of the Ni-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) was 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 (λ = 1.5406 Å), 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 JSM5410, 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 Microetrics 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 (1 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 range.
range 10 mHz–100 kHz and using a signal of amplitude 5 mV peak-to-peak. The potential was kept constant (at 0.52 V in this work) for 500 s until constant current (steady state conditions) and then the EIS was measured. Stock solution of 1.5 M urea was prepared in 0.5 M KOH and lower concentrations were prepared by proper dilutions with 0.5 M KOH. The measurements were repeated to test the reproducibility of the results.

3. Results and discussion

3.1. Surface and structural characteristics of N-NiPh

The morphological and structural characteristics of the thus prepared NiPh particles were studied by XRD, SEM and BET measurements. The SEM image of the NiPh particles prepared by the reflux method is shown in Fig. 1. The image reveals a spherical-like shape of the NiPh particles with average size of ~70 nm. It may be concluded that the semi-spheres have almost uniform size distributions.

By an aid of FT-IR absorption spectroscopy, the different functional and structural properties of the NiPh can be discussed as presented in Fig. 2. As revealed by the figure, there are a set of bands corresponding to different functional groups which may be discussed as follows. The figure reveals three vibrational broad bands in the range of 3000–3450 cm\(^{-1}\) (from 1 to 2 peaks) which are assigned to the O-H stretching vibration of the H\(\text{2O}\) that will be validated by XRD (c.f. Fig. 3). The bending vibrational mode of water molecules appear at 1592 cm\(^{-1}\) (peak 3) [35,36]. The band assigned at 740 cm\(^{-1}\) (peak 3) is attributed to the librational modes of water molecule. Based on literature those bands were disappeared when the nickel phosphate powdered materials were calcined at higher temperature [37]. The vibrational bands of PO\(_4^3-\) anion are observed around 1072, 1022, 991 and 883 cm\(^{-1}\) (peaks 4, 5, 6 and 7) [35,36]. Those bands are corresponding to the tetrahedral PO\(_4^3-\) stretching vibrations and the strong band found at ~580 cm\(^{-1}\) (peak 9) is assigned to P-O vibrations.

The XRD pattern can be used to confirm and determine the chemical structure of the synthesized NiPh. This is demonstrated in Fig. 3. The XRD results demonstrate that the chemical identity of the nickel phosphate is Ni\(_3\)(PO\(_4\))\(_2\).8H\(_2\)O with a monoclinic crystallographic form. The crystallinity and purity of the nickel phosphate sample were examined by X-ray diffraction (XRD) pattern. The XRD pattern consists of sets of peaks which correspond to the N-NiPh. The characteristic peaks of NiPh appear at different 2\(\theta\) values. Those peaks are indexed to the monoclinic crystalline structure of Ni\(_3\)(PO\(_4\))\(_2\).8H\(_2\)O in accordance with that of the standard spectrum (PDF No. 33–0951) [38]. The XRD pattern shows that the samples are single phase structure.

The average grain size \(D\) is estimated by means of the Scherrer formula [39].

\[
D_{hkl} = \frac{k \lambda}{\beta \cos \theta}
\]

where, \(D_{hkl}\) is the average crystallite size, \(k\) is a constant shape factor = 0.9, \(\beta\) is the full width at half maximum, \(\lambda\) is the wavelength of the X-ray radiation, \(\theta\) is the angle of diffraction. The average grain size \(D_{hkl}\) is estimated to be 51.0 nm for the NiPh prepared by the present experimental conditions. The surface area of the N-NiPh powder was given by BET method. The BET analysis results for the nickel phosphate obtained via reflux method are given here. The prepared sample has specific surface area of 22.3 m\(^2\)/g. The total pore volume and the average pore size for the produced nickel phosphate powdered were \(6.85 \times 10^{-3}\) cm\(^3\)/g and 12.3 nm respectively.

3.2. Electrochemical characteristics of GC/N-NiPh

The electrochemical characteristics of N-NiPh modified electrode can help in understanding the redox property of the NiPh and also to understand its electrocatalytic properties. Hence in this section, a light is going to be thrown on this issue. Fig. 4-I shows...
In the coming text, we are going to denote $\text{Ni}_3(\text{PO}_4)_2$ and $\text{Ni}_3(\text{OH})_2(\text{PO}_4)_2$ as Ni(II) and Ni(III), respectively. The continuous increase in the enrichment is accompanied by continuous increase in the surface concentration of the active Ni species in the NiPh matrix and hence an increase in the current. After reaching to a saturation level of the surface layer of the N-NiPh with the nickel redox species and the diffusion of the $\text{OH}^-$ becomes a controlling factor, no further increase in the current is observed. The enrichment of the NiPh matrix with the Ni(II)/Ni(III) species and the increase in current can also be verified by electrochemical impedance measurement before and after the potential cycling shown in Fig. 4-I. Fig. 4-II shows Nyquist plots for the GC/N-NiPh at $E = 0.52 \text{ V}$ before (A) and after (B) potential cycling (75 cycles) of the GC/N-NiPh. The Nyquist plot in Curve A shows tilted straight line while Nyquist plot (after cycling, Curve B) reveals a depressed semicircle. No obvious semicircle was observed in Curve A. This may be attributed to the low conductivity of the GC/N-NiPh matrix before cycling. This is consistent with the obtained low currents in curve “a” of the CVs in Fig. 4-I. This behavior is often shown on oxide films and on low conductivity matrix [41,42]. This denotes low concentration of the Ni(II)/Ni(III) species in the case of GC/N-NiPh before cycling compared to the case of Curve B (after potential cycling). This result demonstrates high charge transfer rate after potential cycling compared to that before the cycling process. The impedance parameters (e.g., charge transfer resistance, $R_{ct}$) were obtained by fitting the experimental EIS data to a model with elements found in the inset of Fig. 4-II. A simulation of the impedance data in Fig. 4-II is performed by replacing the capacitor, C with the CPE in the equivalent circuit (inset of Fig. 4-II). This is in agreement with the approaches found in literatures [43,44]. The use of CPE in modeling is to account for frequency dispersion behavior corresponding to some physicochemical processes such as surface inhomogeneity resulting from surface roughness, distribution of the active sites, dislocations, impurities and possible adsorption process [43,44]. The $R_{ct}$ values before and after the potential cycling were found to be $2.30 \times 10^5$ and $2.77 \times 10^3 \Omega \text{ cm}^2$, respectively. Thus, the $R_{ct}$ value after is much less than that before the potential cycling process. These values demonstrate the large enhancement and the easiness of charge transfer at the electrode/solution interface upon potential cycling in the alkaline solution.

After the above potential cycling, the CV responses were recorded for the GC/N-NiPh in 0.5 KOH at different scan rates in the range of 5 mV s$^{-1}$ to 400 mV s$^{-1}$. This is shown in Fig. 5A. The anodic and cathodic peak currents increase with the scan rate. The anodic peak potential shifts to more positive values where the cathodic peak potential shifts to less positive values. This points to the quasi-reversible nature of the Ni(II)/Ni(III) transform process. A plot of the anodic peak current, $I_{pa}$ and cathodic peak current, $I_{pc}$ of the Ni(II)/Ni(III) transform with the scan rate, $v$ are shown in Fig. 5B. The data were extracted from the CVs shown in Fig. 5A. The obtained straight lines in Fig. 5B demonstrate that the Ni(II)/Ni(III) transform is a surface-confined process. The surface concentration is the electroactive surface coverage (in mmol cm$^{-2}$) of the active nickel-containing species at the electrode surface ($\Gamma$) and it was estimated by using the equation:

$$\Gamma = \frac{Q_{ct}}{nF}$$

where $Q_{ct}$ is the charge passed during the Ni(II)/Ni(III) transform, $n$ is the number of electron and $F$ is Faraday’s constant. The quantity of charge, $Q_{ct}$ was estimated by integrating of the area under the anodic sweep at scan rate of 5 mV s$^{-1}$ in Fig. 5A. This was estimated.
for the Ni(II)/Ni(III)Ph (n = 3, see Eq. (2)). The value of \( G \) is found to be 1.95 \( /C_2 \) 10 \( /C_0 \) 4 mmol cm \( /C_0 \) 2 for the Ni(II)Ph/Ni(III)Ph at the present loading level (3.0 mg cm \( /C_0 \) 2). The loading level in mg cm \( /C_0 \) 2 can be estimated from the above value of \( G \) using the formula:

\[
\text{Estimated loading (mg cm}^{-2}\text{)} = G \times M(\text{NiPhAvg})
\]

where \( M(\text{NiPhAvg}) \) is the average molar mass in g/mol for the nickel species. It was taken as an average between the \( \text{Ni}_3(\text{PO}_4)_2 \) and \( \text{Ni}_3(\text{OH})_3(\text{PO}_4)_2 \). The loading level estimated from Eq. (4) is 0.0796 mg cm \( /C_0 \) 2. This value is much less than the real loading level (3.0 mg cm \( /C_0 \) 2) and yet the percentage utilization ([Estimated loading/real loading]x100) is –2.57%. This value demonstrates the surface nature of the activation and penetration extent. Also, we may conclude that the conversion of the NiPh to the various redox couples is limited to some surface layers.

### 3.3. Electrocatalytic oxidation of urea

In this part, the electrochemical oxidation of urea on the GC/N-NiPh from alkaline 0.5 M KOH is studied at different experimental conditions using cyclic voltammetry. Fig. 6 depicts CV responses of GC/N-NiPh in 0.5 M KOH (a) and in 0.5 M KOH containing 0.3 M urea (b) at scan rate of 20 mV s \( /C_0 \) 1. The CV in blank shows one anodic peak at 0.52 V and one cathodic peak at 0.38 V. These correspond to the redox transform of Ni(II)/Ni(III) species as discussed in the previous section (see Fig. 5A and Eq. (2)). The CV response in presence of urea has different features. The anodic peak current in presence of urea increases dramatically to much higher values at potential higher than that in blank which assigned for the electrochemical oxidation of urea which is coinciding with the Ni(II)/Ni(III) transform. The anodic peak, \( E_p \) in presence of urea is ~0.61 V. In the reverse scan, an anodic peak is revealed at 0.59 V with lower peak current than that in the forward sweep. This can be attributed...
to further oxidation of urea due to recovery of Ni(II)/Ni(III) active sites on the GC/N-NiPh surface. However, this anodic peak current is still lower than that obtained at the forward direction indicating uncompleted recovery of the active sites. The cathodic peak is significantly diminished to much lower currents than that in the blank. This is assigned for irreversible nature of urea oxidation on the GC/N-NiPh electrode. This may suggest electrocatalytic oxidation mechanism of urea on the GC/N-NiPh electrode [45,46]. Study of the stability of electrocatalyst is considered to be a crucial matter in the field of electrocatalytic oxidation of small organic compounds for possible use in fuel cells and biochemical sensors. Fig. 6B shows I-t curve for GC/N-NiPh in 0.5 M KOH containing 0.3 M urea at $E = 0.62$ V. The current increases at the start maybe due to initial activation of the electrode and then it decreases to a constant value. This result denotes continuous enhancement of the urea electrooxidation for considerable duration of ~1.1 h. This suggests remarkable stability of the GC/N-NiPh towards urea electrooxidation at the present experimental conditions.

The oxidation of urea on GC/N-NiPh electrode was illustrated by collecting CV responses at different potential scan rates from 0.5 M KOH containing 0.3 M urea. The CVs are shown in Fig. 7A. The anodic peak current of urea oxidation increases with the scan rate. It is noticed also that the peak potential of urea oxidation shifts to more positive values with the scan rate. Analysis of the data in Fig. 7A can help to extract important parameters and in electrochemical characterization of urea oxidation on GC/N-NiPh. A plot of the peak potential, $E_p$ with the logarithm of the scan rate, $\ln v$ is shown in Fig. 7B. The obtained straight line can be fitted with the following equation [47,48].

$$E_p = K + \frac{RT}{2a_{n_a}} \ln v$$

where $K$ is a constant given by:

$$K = E^0 + \frac{RT}{2a_{n_a}F} \left[0.78 + 0.5 \ln \left(\frac{a_{n_a}FD}{k^2RT}\right)\right]$$

Note that $a$ is the charge transfer coefficient, $n_a$ is the number of
electrons evolved in the rate determining step, $E^0$ is the standard electrode potential, $k$ is the heterogeneous rate constant and $D$ is the diffusion coefficient. From the slope of the straight line shown in Fig. 7B, the obtained value of $\alpha_{ak}$ is found to be 0.683. This value is comparable with that found for urea oxidation on nickel oxide at similar conditions \[49\].

A plot of the peak current estimated from the CVs in Fig. 7A with the square root of the scan rate, $v$, is shown in Fig. 7C. A straight line is obtained in this case \[R^2 = 0.998\]. For completely irreversible process (as evident from the above results), one can use the equation for diffusion-controlled irreversible process which is given by Randles–Sevcik (Eq. (7)) \[45,50\]:

$$I_p = 0.4961 \times n F \left( \frac{\alpha_{ak} F D}{RT} \right)^{0.5} A C v^{0.5}$$ \[7\]

where $I_p$ is the peak current, $n$ is the total number of electrons ($n = 6$, \[49\]), $A$ is the surface area of the working electrode, $D$ is the diffusion coefficient of urea, $C$ is the bulk concentration of urea and $v$ is the potential scan rate. Also, $F$, $R$ and $T$ have their usual meaning. The diffusion coefficient is calculated from fitting of the theoretical plot based on the above Randles- Sevcik equation with the experimental data and it was found to be $D = 7.1 \times 10^{-6}$ cm$^2$ s$^{-1}$ using when $A = 0.0314$ cm$^2$ and $\alpha_{ak} = 0.683$ (as determined from Fig. 7B). This value of $D$ is comparable with the values reported in literatures at similar conditions \[51\]. A plot of $I_p v^{0.5}$ with the scan rate as shown in Fig. 7D exhibits the characteristics features of typical catalyst regeneration mechanism. This can be suggested in the light of possible catalyst regeneration mechanism during the electrocatalytic oxidation of urea on the GC/Ni-NiPh \[34\].

Fig. 8 depicts the effects of the urea concentration on the CV response of the GC/N-NiPh in 0.5 M KOH containing different concentrations of urea at scan rate of 20 mV s$^{-1}$. As the urea concentration increases the peak current increases with urea concentration before it reaches constant value at [Urea] $\geq$ 0.75 M. The inset of Fig. 8 shows the relation between $I_p$ and the [urea]. It can be seen that $I_p$ increases linearly up to [urea] = 0.3 M before it tends to have different regime at higher concentrations. This may be attributed to a diffusion-controlled process at [urea] $\leq$ 0.3 M. At higher concentrations, the peak current tends to have independent behavior from the urea concentration pointing to some kinetics limitation of the urea oxidation process \[52\]. The above tendency of the $I_p$ with [urea] $>$ 0.3 M can be discussed as follows. The competitive adsorption of urea molecules with the OH$^-$ ions on the GC/Ni-NiPh surface may favor the urea molecules coverage on the electrode surface which hinders the adsorption of OH$^-$ which has an essential role in the oxidation of small organic molecules on the electrode surface \[53\].

### 3.4. Origin of the enhancement of urea oxidation

As discussed in literatures and evident from our work here, the electrooxidation of urea and other small organic compounds follows a catalyst-regeneration mechanism. This implies the production of a redox system, (Ni(II)/Ni(III)) \[Ni(II)Ph/Ni(III)Ph\] in our case here and enrichment of the catalyst surface layer with these species. Urea molecule combine with species of higher oxidation state (Ni(III)) converting them to lower oxidation state (Ni(II)) which is re-oxidized to give the one of higher oxidation state. In this context and before potential cycling the NiPh does not have this enrichment of the different redox species of Ni(II) and Ni(III) and yet potential cycling was essential to reach to this high surface concentration (see Fig. 1). Accordingly, this mechanism can be written as \[54,55\].

At the anode:

$$E^{0} \quad 2\text{Ni(II)} + 6\text{OH}^- \rightleftharpoons 2\text{Ni(III)}\text{(OH)}_3 + 6\text{e}^-$$ \[8\]

$$C \quad 2\text{Ni(III)}\text{(OH)}_3 + \text{CO(NH}_2)_2(aq) \rightarrow 2\text{Ni(II)} + \text{N}_2(g) + \text{CO}_2(g) + 5\text{H}_2\text{O}(9)$$

Net anodic reaction:

$$EC' \quad \text{CO(NH}_2)_2(aq) + 6\text{OH}^- \rightarrow \text{N}_2(g) + \text{CO}_2(g) + 5\text{H}_2\text{O} + 6\text{e}^-$$ \[10\]

Hence, Ni(II) is anodically converted to Ni(III) and consequently the catalytically active Ni(III) is chemically reduced to the inactive Ni(II) as a result of urea oxidation. Meanwhile, urea is chemically oxidized to products. The inactive Ni(II) will be electrochemically oxidized to Ni(III) due to the prevailing high oxidation potential thus regenerating the catalyst for further oxidation of urea molecules. This is in accordance with the results shown in Fig. 6. Under the present conditions, NiPh worked as a good electrocatalyst for urea oxidation in alkaline solutions. The obtained catalytic activity of the N-NiPh electrode here in this work towards urea oxidation may be compared with the results obtained for Ni-based modified electrodes at similar conditions \[29,49,55–57\]. Table 1 lists this comparison and specifications of the works in the given references.

**Table 1**

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<th>Material</th>
<th>This work</th>
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<th>[49]</th>
<th>[55]</th>
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$^a$ SS: stainless steel.
at similar operating conditions\footnote{29,51,55–57} with our work here. The specific activity, given in m\AA\ cm\textsuperscript{2} mg\textsuperscript{-1} of the catalyst, in our work is almost equal in some cases\footnote{55} and higher in other cases\footnote{29,49,56,57}. Hence, we may say that our electrode is superior to many Ni-based electrodes. This may be attributed to the high adsorbability of the phosphate ions, PO\textsubscript{4}\textsuperscript{3\textendash}}, to the small organic compound and better stability of the N-NiPh\footnote{58,59} which are advantages for using NiPh as an electrocatalyst. Also, presenting new catalyst (NiPh) for oxidation of small organic molecules (important catalytic reaction in fuel cells and biosensors) may present a valuable contribution. On oxidizing Ni(II) to Ni(III) within (important catalytic reaction in fuel cells and biosensors) may new catalyst (NiPh) for oxidation of small organic molecules advantages for using NiPh as an electrocatalyst. Also, presenting chemical structure of Ni\textsubscript{3}(PO\textsubscript{4})\textsubscript{2.8}H\textsubscript{2}O. The N-NiPh demonstrates a nanoscale of ~70 nm with monoclinic crystallographic form and considering that Ni(II)/Ni(III) active sites may be more stabilized due to the backbone of the phosphate structure\footnote{17,59}.

4. Conclusions

NiPh was synthesized for the first time by a simple reflux method and its morphology and structure were characterized. The material was characterized by SEM, XRD, FTIR and BET measurements. The synthesis process gave semi-spherical particles with material was characterized by SEM, XRD, FTIR and BET measurements. The synthesis process gave semi-spherical particles with invasion of OH\textsuperscript{\textendash} ions and formation of Ni(II)/Ni(III) Ph. The GC/N-NiPh reveals good electrocatalytic properties towards urea oxidation from 0.5 M KOH. The electrocatalytic reaction was analyzed in the light of the collected experimental data. The material may need further modification by controlling the experimental conditions to obtain materials with better morphology and better catalytic activity.

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