



# Nickel nanoparticles-decorated graphene as highly effective and stable electrocatalyst for urea electrooxidation

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## ABSTRACT

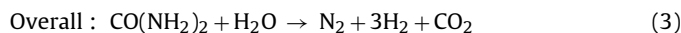
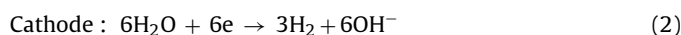
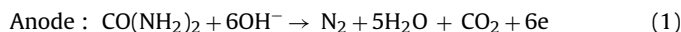
Among the various carbonaceous materials, graphene is highly considered to provide the optimum support for the electrocatalytic materials due to its excellent electrical conductivity and extremely large surface area. In literature, based on our best knowledge, few studies have been reported to introduce effective electrocatalysts for urea oxidation. In this study, Ni-decorated graphene sheets are introduced as effective and stable electrocatalyst for urea oxidation. The introduced composite was prepared by reflux of graphene oxide with nickel acetate at 120 °C for 10 h followed by calcination in argon atmosphere at 850 °C for 2 h. X-ray diffractometer (XRD), transmission electron microscope (TEM) and Raman spectroscopy techniques confirmed formation of graphene sheets decorated by nickel nanoparticles. The synthesized Ni-decorate graphene shows distinct electrocatalytic activity toward urea oxidation. Numerically, using 2 M urea solution (in 1 M KOH) the corresponding current density was 150 mAcm<sup>-2</sup> (2100 mAcm<sup>-2</sup> g<sup>-1</sup>) with clear urea oxidation peaks in the forward and reverse scans. Study the influence of metal loading indicated that the amount of nickel nanoparticles should be optimized as the best performance has been observed when equal amounts of nickel acetate and graphene oxides were utilized during the preparation process. The introduced decorated graphene reveals good stability at various applied voltages. Overall, the study emphasizes the advantage of using graphene as support to distinctly enhancing urea electrooxidation.

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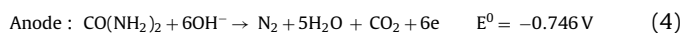
## 1. Introduction

Due to the relatively high hydrogen content in urea, urea-rich wastewaters can be manipulated as an energy source. Either hydrogen or electricity can be generated from this valuable wastes by electrolysis or urea-based fuel cell, respectively. Electrolysis has previously been proposed to directly convert urea to hydrogen

through electrochemical oxidation according to the following reactions [1–4]:

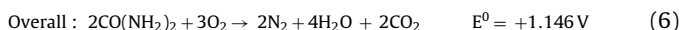


Because urea contains a relatively high amount of hydrogen (10 wt%), so it be given the proper attention as an effective hydrogen storage material. Moreover, compared to compressed and liquid hydrogen, urea possesses higher energy density. The equivalent energy densities of urea, compressed hydrogen (at 700 bar) and liquid hydrogen are 16.9, 5.6 and 10.1 MJl<sup>-1</sup>, respectively [5]. On the other hand, urea-rich wastewaters can be used directly in a fuel cell to generate electricity according to the following reactions [5].



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However, the membrane should be optimized in order to avoid carbonization of the membrane in the alkaline medium.

It was found that, even compared to precious metals, nickel displays better performance as an anode in both fuel cells and electrolysis process. Compared to noble metals, nickel catalysts showed higher current densities and lower oxidation potentials for the electro-oxidation of urea [1]. As electrolysis of urea should be conducted in alkaline medium, and its corresponding fuel cannot be run in acidic conditions, Ni-based materials possess good chance to be utilized as anodes due to the good chemical stability. However, the gap between the theoretical ( $-0.46\text{ V}$  vs. SHE) and the observed (ca.  $0.45\text{ V}$  vs. SHE) electrooxidation potential of urea over the nickel catalysts is significant. Therefore, research is being conducted to develop novel nickel catalysts based on the modification of the morphology or chemical composition of the electrocatalysts. Some reports have been presented including work on a nickel-carbon sponge [6], nickel nanoribbons [7], nickel nanowires [8,9], and nickel nanoparticles [10]. In addition, trials have been performed to exploit the synergetic effect of Ni-based alloys including Ni-Co [2], Ni-Mn [11] and Ni-Zn [12].

Besides the good electrical conductivity and high chemical resistance, the adsorption capacity of the carbonaceous materials makes them optimum supports for functional electrocatalysts; especially, the oxidation reaction is considered to be a combination of adsorption and electrochemical processes [13,14]. The high surface area and excellent electrical conductivity gives graphene the advantage of being an optimum support material. Accordingly, in this study, Ni-decorated graphene was prepared and investigated as an electrocatalyst for urea oxidation. The results are satisfactory, as a very high current density was observed compared to the reported nickel-based catalysts.

## 2. Experimental work

### 2.1. Materials

The utilized metallic precursor in preparation of the introduced Ni-decorated graphene was nickel acetate tetrahydrate (NiAc, 99.0% assay, Sigma Aldrich) which was utilized without any further modification. However, graphene was synthesized using graphite powder ( $<20\ \mu\text{m}$ ), hydrogen peroxide, hydrazine monohydrate and sulphuric acid (95–97%) which were purchased from Sigma–Aldrich. Distilled water was used as a solvent.

### 2.2. Procedures

#### 2.2.1. Preparation of graphene oxide (GO)

Graphene was prepared chemically from reduction of exfoliated GO. The GO was synthesized from natural graphite powder using a modified Hummer's method [15,16]. Briefly; 5 g of graphite treated twice with 5% HCl was placed in cold ( $0^\circ\text{C}$ ) concentrated  $\text{H}_2\text{SO}_4$  (130 ml), then 15 g of  $\text{KMnO}_4$  was added gradually to the mixture which is being kept in an ice bath with stirring for 2 h. After dilution with deionized (DI) water, the temperature was increased to  $98^\circ\text{C}$ . The mixture was then cooled to room temperature and  $\text{H}_2\text{O}_2$  (50 ml, 30 wt.%) was added; the mixture was then left overnight. The mixture was filtered under vacuum and the obtained precipitate was washed with 10% aqueous HCl several times and dried at  $50^\circ\text{C}$ .

#### 2.2.2. Preparation of Ni-loaded graphene

In 250 ml round flask, 300 mg of the prepared GO was dispersed in 400 ml distilled water and ultrasonicated for 40 min; 0.5 ml of

hydrazine hydrate was then added to the suspended GO. Specific amount from NiAc was dissolved individually in the minimum amounts of water and mixed with the GO suspension. Typically, to study the influence of metal loading, 100, 200, 400 and 600 mg NiAc were utilized. In other words, the prepared samples have 25, 50, 100, and 150 wt.% NiAc with respect to the solid GO. The slurry was then refluxed at  $150^\circ\text{C}$  for 10 h. Later on, the solution was filtered. The obtained filter cake was then washed several times by plenty amounts of DI water, dried under vacuum at  $80^\circ\text{C}$  for one night, and then calcined under argon atmosphere at  $850^\circ\text{C}$  for two hours. [17–20]. Moreover, calcination of GO leads to decrease the weight  $\sim 50\%$  [21,22]. Accordingly, the aforementioned NiAc percentages with respect to GO can be determined to be 11.8, 23.6, 47.2 and 70.8 wt.% nickel nanoparticles with respect to graphene. However, hereafter, the NiAc to GO ratio will be used.

### 2.3. Characterization

Information about the phase and crystallinity was obtained by using Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with  $\text{Cu K}\alpha$  ( $\lambda = 1.5406\ \text{\AA}$ ) radiation over Bragg angle ranging from  $10$  to  $100^\circ$ . Normal and high resolution images were obtained with transmission electron microscope (TEM, JEOL JEM-2010, Japan) operated at 200 kV equipped with EDX analysis. The Raman spectra were measured using Nanofinder 30 spectrometer (Tokyo Inst. Co., Japan) equipped with a He:Ne ( $\lambda = 633\ \text{nm}$  laser) and the scattering peaks were calibrated with a reference peak from a Si wafer ( $520\ \text{cm}^{-1}$ ). Raman spectra were recorded under a microscope with a  $40\times$  objective in range of  $0$ – $1600\ \text{cm}^{-1}$  and 3 mW of power at the sample. The electrochemical measurements were performed on a VersaSTAT 4 (USA) electrochemical analyzer and a conventional three-electrode electrochemical cell. A Pt wire and an Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively. All potentials were quoted regarding to the Ag/AgCl electrode. Glassy carbon electrode was used as working electrode. Preparation of the working electrode was carried out by mixing 2 mg of the functional material, 20  $\mu\text{L}$  Nafion solution (5 wt%) and 400  $\mu\text{L}$  isopropanol. The slurry was then sonicated for 30 min at room temperature. 15  $\mu\text{L}$  from the prepared slurry was spilled on the active area of the glassy carbon electrode which was then subjected to drying process at  $80^\circ\text{C}$  for 20 min. The active surface area of the utilized glassy carbon working electrode was  $0.07\ \text{cm}^2$ . Actually, the normalization was estimated based on the active surface area of the working electrode. The functional material weight used on the prepared electrode was 0.07143 mg.

## 3. Results and discussion

### 3.1. Characterization of the prepared electrocatalyst

#### 3.1.1. Raman spectroscopic analyses

To properly investigate the composition of the introduced material, pristine graphene has been prepared first to check the efficiency of the utilized procedure in formation of graphene. Raman microscopy can provide a trustable comparison between graphite, GO and graphene. For instance, graphite displays a prominent G peak at  $1581\ \text{cm}^{-1}$ , corresponding to the first-order scattering of the E<sub>2g</sub> mode [23]. However, in the Raman spectrum of GO, the G band is broadened and shifted to  $1594\ \text{cm}^{-1}$ . Moreover, because of the reduction in size of the in-plane sp<sup>2</sup> domains due to the extensive oxidation, the D band at  $1363\ \text{cm}^{-1}$  becomes prominent. On the other hand, the Raman spectrum corresponding to graphene contains both G and D bands (at  $\sim 1580$  and  $\sim 1350\ \text{cm}^{-1}$ , respectively) with an increase in the D/G intensities ratio compared to that in GO. This change suggests a decrease in the average size of the sp<sup>2</sup>

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