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# Enhanced electrocatalytic activity towards urea oxidation on Ni nanoparticle decorated graphene oxide nanocomposite

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## Abstract

Hydrogen production from natural resourses and industrial waste water is of vital and duel importance to the energy and environmental issues. Urea oxidation based on cost effictive catalyst and which is substuation to the noble based electrolysers like Pt, Pd and Rh of great challange. Herein, we have fabricated effective decoration of Ni NPs on GO by chemical reduction approach and characterized by Furrier transfarm infra red (FTIR) spectroscopy, X-ray diffraction (XRD), transmissio electron microscopy (TEM), Raman spectroscopy, BET surface area measurements and X-ray photoelectron spectroscopy (XPS). In the morphological studies TEM confirms the Ni NPs (~10nm) on GO (~20nm thickness) and XRD confirms its FCC crystal structure. Further, Raman spectroscopic analysis showed the increment of $I_D/I_G$ ratio more than double in GO compared to Ni@GO supports decoration of Ni NPs on GO. BET analysis also supports Ni@GO having higher surface area compared to Ni NPs and GO individuals, More significantly, binding energy of Ni is zero-valent confirmed from XPS of Ni@GO. Electrochemical activity of Ni@GO from cyclic voltammetry (CV) shows the ultrahigh current density is of 27 $mA/cm^2$ at an ultralow onset potential of 0.30V vs SCE having long term stability. Electrochemical impedance spectroscopy (EIS) shows the highly sensitive towards the urea oxidation

reaction on Ni@GO nanocomposite. The electrocatalytic activity on Ni@GO is pH sensitive towards urea oxidation.



## Introduction

Increasing energy demand due to improved traditional life style worldwide along with growing population hence community facing with serious environmental issues including pollution, global warming and many more [1a]. Amongst the existing renewable resources of energy as an energy storage material [1b], fuel [1c] and hydrogen as consider to be cleanest fuel compared to other energy resources. Unfortunately, large scale utilization of $H_2$ reserved further because of safety issues for transportation and even for storage. To overcome these problems traditionally used hydrogen rich fuel resources includes ethanol, formic acid, formaldyde, ascorbic acid, methanol, hydrazine, urea, ethylene glycol and other low molecular weight organic species in fuel cells and other conversion engines. For example, direct methanol fuel cells (DMFCs), direct ethanol fuel cells (DEFCs), direct urea fuel cells (DUFCs) and others [2]. Moreover, urea provides features including clean, nontoxicity, non-flammable nature and especially long-time supply of the $H_2$ because of having natural abundance, features. The resources for urea includes urea rich waste water from fertilizer industries, human/animal urine and other wastes. Those natural waste materials are typically introduced for futuristic ways for electrocatalytic $H_2$ production [2,3]. On the other side, it also solves environmental issues like its by-product supplies hydrolyse pollutants such as ammonia and nitrate mixture with drinking water and it is having serious effects on human health. Hence, to resolve those issues electrochemical urea oxidation gives multiple solutions including $H_2$ production, environmental protection and also as a direct fuel for fuel cells i.e. DUFCs [4a]. However, $H_2$ production via. Water splitting (through both water reduction i.e. HER and oxidation i.e. OER) is cleanest source of $H_2$ and also having natural abundance of water is 70–75%. Eventhough, for oxidation of water requires higher potential with complex six electron transfer reaction and it limits the overall $H_2$ production. More significantly, MacFarlane et al., reported electrochemical oxidative conversion of urea (0.37V vs. SCE) into $H_2$ required less potential compared to water electrolysis which could be due to absence of OH bond, which is difficult breaking of and formation of $O_2$ molecule (1.23V vs. SCE). Unfortunately, HER from water needs of 70% higher energy

compared to from urea [4b]. For example, Lan et al. and Manthiram et al. studied urea electrolysis on Ni/C and Ni NPs catalyst and are found to be maximum power densities i.e. 1.7 $mW/cm^2$ and 14.2 $mW/cm^2$ respectively in alkaline medium [2,3]. Accordingly, energy efficient and earth abundant natural waste representative urea electrolysis is the sluggish kinetic path and having $6e^-$ transfer reaction mechanism [4b]. Literature reflects efficient electrocatalytic systems includes Ti-Pt [5], Ti-(Pt-Ir) [6] and Ru-$TiO_2$ [7] and are having better stability and activity in neutral medium. But its large scale production restricted by the use of expensive noble metals like Pt, Ru, Ir etc. Also having surface poisoning issues at electrified interfaces which further hampers electron transfer processes. To solve these issues and make the system cost effective researcher have developed electrocatalytic systems using earth abundant metal/metal oxides, alloys, hybrids with carbon based nanostructures. For example, Ni and Ni based catalyst is found tobe admirable and highly active electrocatalytic system for urea oxidation. However, Ni based electrocatalysts loses their electrocatalytic activity, if you used for longer time due to surface oxidation of Ni atoms. In this line, to further improves the long term current and potential stability towards urea oxidation, different groups in literature have tried doping of another metals with Ni based bimetallic and/or their carbon based nanocomposites, for example, Ni-Fe [8], Ni-Pd@carbon nanofiber [9], and $MoS_2$/$NiS_2$ [10].

Among these $MoS_2$/$NiS_2$ is widely used as a multifunctional electrocatalytic system for both HER and OER, supercapacitor and microwave absorption studies. Moreover, Botte and co-workers reported use of Raman spectroscopic analysis for the indirect chemical and electrochemical urea oxidation along with proposed mechanistic pathway on Ni [6]. Accordingly, urea transformed into $N_2$ (g), $H_2$ (g) and $CO_2$ (g) and catalyst $Ni(OH)_2$ converts into Ni oxy-hydroxide species during it's oxidation. Additionally, role of carbon nanotube (CNTs), graphene, carbon black, $C_{60,}$ carbon nitride, and polyaniline are found tobe excellent support used for decoration of metal/metal oxide NPs of different shapes .

Since, last two decades graphene and its various analogues has received great attention, owing to its large specific surface area, high and further tuneable electrical conductivity and superior chemical stability. Hence, it promotes its wider use as a conducting support, because of having $sp^2$ carbon centres results into increasing e-conjugation and also largely available anchoring sites to load metals/composites. For example, it has received great attention as an efficient support and has been widely used and reported in photoelectric devices i.e. $CsPbBr_3$@GO, AgInZnS/GO, $Cu_2O$/rGO [[11], [12], [13], [14]]. Accordingly, herein we report on synthesis of Ni@GO by using simple chemical synthetic approach having flower like features and is highly active for electrocatalytic urea oxidation at ultralow overpotential of 0.30V vs. SCE in alkaline medium. These results further demonstrates the simple synthetic approach which proven tobe suitable for controlled decoration of Ni NPs on GO with improved electrocatalytic activity towards urea oxidation and found tobe better than similar reports from literature. .

## Section snippets

## Material

Graphite powder (45 μm, >99.99 wt %), nitric acid (70.4%), sulphuric acid (98%), hydrochloric acid were all purchased from Sigma-Aldrich. Whereas, absolute ethanol (99.99%), nickel chloride ($NiCl_2$. $6H_2O$), ammonia, hydrazine hydrate were purchased from Fischer scientific. All the chemical reagents were of analytical grade and used as received without further purification. Deionized water was used as a solvent throughout the synthesis of the materials as well as for electrochemical and…

## Results and discussion

Morphological characterization of Ni@GO and GO is carried out by transmission electron microscopy (TEM) and is shown in Fig. 1(a). Accordingly, TEM image of GO (~20 nm width) shows the few layer of graphene and wrinkled surface to provide the higher stability for Ni NPs i.e. NI@GO shown in Fig. 1(b). Moreover, HR-TEM shown in Fig. 1(c) of Ni@GO nanocomposite having average size of Ni NPs is 10 nm with uniform growth GO having flower like shape with porous nature which could be responsible for…

## Conclusion

The Ni@GO electrocatalyst synthesized by using simple chemical reduction method. As-synthesized nanocomposite along with Ni NPs have been well characterized by FTIR was confirms the Ni-C bonding in Ni@GO. The elemental analysis by using the EDAX shows the only Ni, C and O elements present in Ni@GO. XRD shows the Ni NPs in Ni@GO is having FCC structure and Raman spectroscopic analysis shows the $I_D/I_G$ ratio increases in Ni@GO as compared to GO, it confirms there is an increment in $Sp^2$ carbon. TEM …

## CRediT authorship contribution statement

**Ajay V. Munde:** Methodology, Validation, Investigation, Writing - review & editing. **Balaji B. Mulik:** Validation, Investigation. **Parag P. Chavan:** Validation, Investigation. **Bhaskar R. Sathe:** Conceptualization, Methodology, Writing - original draft, Formal analysis, Writing - review & editing, Supervision, Funding acquisition.…

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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