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# Stable and highly efficient Co–Bi nanoalloy decorated on reduced graphene oxide (Co–Bi@rGO) anode for formaldehyde and urea oxidation reactions

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## Highlights

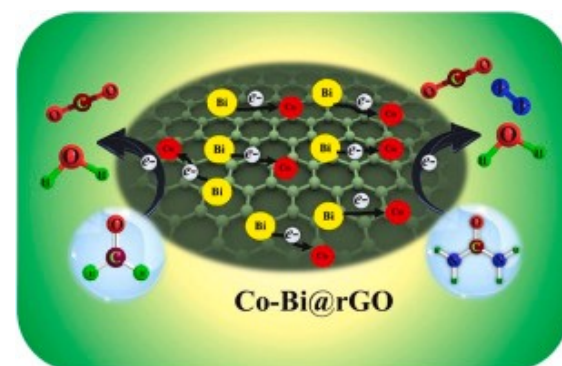
- CoBi@rGO electrocatalyst was synthesized via. electroless exchange method.
- Co and Bi show a promotional as well as cooperative role toward the urea and formaldehyde oxidation.
- Bi plays important role in stabilizing oxygen intermediate, synergetic effect and is helpful for the oxidation reaction.
- CoBi@rGO exhibits high electrochemical activity compared to Co@rGO, Bi@rGO, and GO.

## Abstract

Extremely energetic and low-cost novel nanoelectrodes for fuel cell reactions are always important

for examining more elaborative electrochemical studies at interfacial electron transfer reactions. Herein, this work demonstrated a bifunctional electrocatalyst with its oxophilic character and promoting the role of p-electrons of Bi to be supported with Co (nanoalloy) and further decoration on reduced graphene oxide i.e. Co–Bi@rGO presenting as an auspicious electrochemical activity towards formaldehyde and urea oxidation reactions. Synthesized Co–Bi@rGO composite have been well characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), BET surface area measurement, and X-ray photoelectron spectroscopy (XPS) studies, etc. Further, the electrochemical evaluation shows exceptionally higher activity towards formaldehyde and urea oxidation reactions having onset potential of 0.32V, 0.35V vs. SCE respectively. Interestingly, ultra-high enhancement factor for Co–Bi@rGO could be initiated from the cooperative role of Bi with Co centres, assisting for formaldehyde and urea oxidation reactions. Electrochemical impedance spectroscopy (EIS) and chronoamperometry (i-t) studies using Co–Bi@rGO nanocomposite shows excellent long-term current/potential stability with lower charge transfer resistance towards the formaldehyde and urea molecules. This work deals with practical information for the build of a stable and proficient electrocatalyst for direct formaldehyde and urea fuel cells and also will extendable towards the industrial waste water treatment.

## Graphical abstract



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## Introduction

A revolution as developed countries demands the regular increasing the energy calls and unfortunately causes irreversible environmental issues from the over uses of fossil energy (petrol, diesel, and coal) based resources and major contributor includes transportation, industrialisation, living standard, etc [1,2]. More importantly, environmental concerns about the use of carbon based sources for energy have led to a significant increase in the concentration of greenhouse gases, including CO<sub>2</sub> and SO<sub>2</sub>, which have serious implications for the environment and human health

[3,4]. To resolve these issues, literature reflects the different clean fuel strategies have been developed on high energy density constructed like  $H_2$  come from naturally, waste material, as well as bio-agricultural i.e. ethanol, urea, ammonia and others [5,6]. Recently, economical and sustainable methodology for  $H_2$  and  $O_2$  was exposed to electrochemical  $H_2O$  splitting reactions. The electrochemical  $H_2O$  oxidation is a more complex reaction, because of breaking the OH bond and forming the  $O_2$  molecule requires a larger potential (1.23V vs. SHE), and hence it motivates to find an additional path of the reaction which for replacing OER by the oxidizable anodic reactions. Produced at a low molecular weight of organic molecules, to reduce at exceptionally lower potential (0.37V vs SHE), results into the production of molecular  $H_2$  species from hydrogen rich molecules (methanol, ethanol, formaldehyde, ethylene glycol, urea, furfural, hydrazine, and ammonia) by oxidation reactions using nano-electrocatalysts [7,8].

Of these, urea and formaldehyde are present in the fertilizer industrial waste and also in the air [9]. Interestingly, urea and formaldehyde are promising species one of the degradation species is  $H_2$  which also gives a solution for water and air pollution. In this line urea oxidation liberates  $N_2$  and  $CO_2$  molecules and requires six electrons for a sluggish pathway with lower thermodynamics and it requires electrocatalysts Pt, Rh, Pd, Ag and their hybrids. These catalysts have been suffering from thoughtful complications like their larger and diverse utilizations, lower abundance and, high cost also Pt-based catalyst surface has been more poisoned by  $O_2$ , CO and HCHO intermediate species and hampers their surface activities at electrified interface [[10], [11], [12]]. Therefore, herein, new efficient, alternative and sustainable electrocatalytic systems such as 3d transition metals i.e. Ni, Co, Au, Pt and incorporating with P-orbital promoters such as Bi, Sn, and Pb have also shown larger active sites, extraordinary structural modifications due to increase in the advanced active sites and it reveals that better performance of the electrochemical activity [6,[13], [14], [15], [16]]. Ni-based electrocatalysts are having comparable electrocatalytic activity indirect fuel cell reactions. Unfortunately, the problem with Ni is having lower conductivity and the dissolution of the NiOOH active layer results into loss of their ultra-lower potential and current density [17]. Literature reflects that the determination of urea on the Ni interface, unfortunately, is hampered by the serious issue whereas, individual Ni sites have low conductivity and urea molecules further in the oxidation reaction, blocking their active site due to loss of their exceptional activity. From this perspective, increasing activity, conductivity, and increasingly accessible sites for urea molecules and conversions to support Ni for different metals or carbon-based materials.

Recently, various reports have shown that Ni-based urea oxidation reactions some have serious problems such as larger potential, low current density and stability, overcoming these problems through Co-based materials used for urea oxidation is now a potential new candidate and exceptional electrochemical activity [[18], [19], [20]]. Also, Co has been declared an important component and outstanding operational site in electrocatalysis, while Co alloys with Cu, Ni, Bi and Sn will be shown effective in the material in an electrocatalytic application, because of their alloys, structural adaptation, synergistic effect, defective site, stability of intermediate, electronic and interface properties [15,16,21,22]. For example, **Johnsson et al.** examined  $CoBiF_2O_2$  for improved

activity towards water oxidation due to Bi having an important role in stabilizing oxygen intermediates and their synergetic effect [22]. **Sesu at el.** reported CoCuBi nanoalloy to further increase the activity of intermediate of Cu–OOH and Bi–OOH towards the methanol oxidation due to its structural and electrochemical properties [23]. Similarly, **Xia at el.**, developed Ni<sub>3</sub>Se<sub>4</sub> based electrocatalytic system whereas, Ni modify Se to act as a superior towards bifunctional electrochemical activity switching from OER to more oxidizable molecules such as oxidation of urea and hydrazine [24]. **Wang at el.**, designed CoMn/CoMn<sub>2</sub>O<sub>4</sub> on basis of Schottky heterojunction electrocatalyst to boost urea and water splitting reactions because of the self-resulting charge transfer on the interface. Accordingly, adsorption of reactant molecule and breaking bonds and generation of H<sub>2</sub> efficiently at their lower potential [25]. **Ding at el.** found the decoration of CeO<sub>2</sub> on NiMoO<sub>4</sub> and Ni-based chalcogenides, nitrides, and phosphides increases the defects and these modifications are further responsible for enhanced electrochemical activities of urea oxidation and water reduction at lower potential [26]. However, **Yu at el.** established Ni–Mo–O nanorods have been higher structure in the metallic state due to increasing efficiency towards urea and water splitting to H<sub>2</sub> cost-effective active approach [27].

Moreover, formaldehyde is another potential fuel species that has been significantly important in fuel cell reactions [28]. Pt, Au, Ag, Pd, and Rh based electrocatalysts are efficient and known for high current density with lower potentials. Formaldehyde electrooxidation produces CO like species and blocks active sites of the above metals and hence decreases the activity [[29], [30], [31]]. To further improve the activity towards oxidation reaction Pt has been further modified by different promoters like Cu, Sn, and In Refs. [32,33]. Interestingly, the role of promoters is to further increase the electrochemical activity along with minimising cost and poisons issues for sustainable utility [15,34]. For example, **Kulandainathan at el.** demonstrated the role of supporting material toward the oxidation of liquid fuels increases the electrochemical activity such as formaldehyde>methanol>ethylene glycol>formic acid [35]. **Barman at el.** optimized synthesis for decoration of nanosized Pt on graphitic carbon nitride to increase the electrocatalytic activity and that could be due to an increase in surface area to mass activity, and CO tolerance [36]. **Chen at el. proposed** Ni dopant on Cu substrate to further increase in activity of formaldehyde oxidation in KOH and KOD electrolytes [37]. The overview of the above-said systems towards urea and formaldehyde oxidation indicates there is an urgent need for further improvement in terms of increase in current density, decrease in onset potential, and long-term stability by using the development of novel operational active sites.

Herein, we report for the first time fusion studies of urea and formaldehyde oxidation by using a new catalytic interface using the Co–Bi@rGO model anode system by using a cost-effective and simplistic synthesis route. The unusual performance towards urea and formaldehyde oxidation especially from their unexpected active operational and hybrid sites, defective centre, and synergetic effect. More elaborately, the mechanistic pathway for the urea and formaldehyde oxidation on a new Co–Bi@rGO electrocatalyst is discussed in more exhaustive.

## Section snippets

### Material

Graphite powder (45 $\mu$ m, >99.99wt%), nitric acid (70.40%), sulphuric acid (98.00%), and hydrochloric acid (35–38%) acetone obtained from (S D Fine Chem Ltd. India) were of analytical grade and used as received without further purification. Absolute ethanol (99.99%) was obtained from Fischer Scientific. Cobalt chloride [(CoCl<sub>2</sub>) $\cdot$ 2H<sub>2</sub>O], bismuth nitrate [Bi(NO<sub>3</sub>)<sub>3</sub> $\cdot$ 5H<sub>2</sub>O], sodium borohydride, urea, formaldehyde and KOH were of analytical grade and used as received without further purification....

### Characterization

As synthesized Co–Bi@rGO nanocomposite the morphological characterisation was confirmed by using high-resolution transmission electron microscopy (HR-TEM) and shown in Fig. 2. Accordingly, the HR-TEM image of reduced graphene decorated with black colour circles of Bi nanoparticles (~9.5 nm) further interconnected Co nanoparticles (~2 nm). Also, HR-TEM has seen homogeneous growth as well as nanoscale synthesis Co–Bi@rGO. In Fig. S-1 shown (i-iii) Co–Bi@rGO, Co@rGO and Bi@rGO nanocomposites have...

### Formaldehyde oxidation

Electrochemical evaluation towards HCHO oxidation of as-synthesized Co–Bi@rGO nanocomposite has been investigated by cyclic voltammetry (CV) and chronoamperometry (i-t) studies in basic medium. Consequently, Fig. 3 (a) demonstrates the superimposed CV for Bi@rGO (i), Co@rGO (ii) in 0.5M KOH and Co–Bi@rGO (iii) without HCHO and Co–Bi@rGO (iv) with 1M HCHO prepared in 0.5M KOH at a scan rate of 50mV/s respectively. The Bi@rGO (i) in a mixture of 1M HCHO in 1M KOH is confirmed...

### Conclusion

We have reported synthesis of Co–Bi@rGO nanocomposite by simple chemical reduction approach for electrocatalytic HCHO and urea oxidation reactions. Synthesized electrocatalyst well characterised morphological characterisation by HR-TEM to confirm nanoscale synthesis Co–Bi NPs decorated on reduced graphene oxide. XRD peak indicates smaller sized Co (2nm) around Bi (9.5nm). BET surface area measurement data signifying that Co–Bi@rGO higher surface compared to Co@rGO, and Bi@rGO these results...

### Author information

The authors declare no competing financial interest....

## Author Contributions

A.V.M. designed and conducted all experiments, B.B.M. took over data analysis and editing, R.P.D. contributed the synthesis and functionalization of graphene oxide and other experiments and BRS proposed and supervised the whole project and funding acquisition and assisted in the writing process and data analysis....

## 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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