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Bismuth oxychloride dispersed on nitrogen doped carbon as catalyst for the electrochemical reduction of CO_2 to formate

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Abstract

Electrochemical reduction of CO_2 has found significant interest for converting CO_2 to useful products and closing the carbon cycle. Recent advances through catalyst development have aided in satisfying the requirements of achieving a high product selectivity, activity and long term stability. Among various industrially valuable products, formic acid has found numerous applications such as in fuel cells and the textile industry. In this work, we report the synthesis of bismuth oxychloride dispersed on nitrogen doped carbon by a facile ion adsorption process using bismuth acetate, hydrochloric acid and urea as precursors and discuss its performance as an electrocatalyst for the electrochemical reduction of CO_2 to formate. The results show that bismuth oxychloride dispersed on nitrogen doped carbon has a good catalytic activity for CO_2 reduction to formate in 0.5 M $KHCO_3$ achieving a maximum faradaic efficiency of 84.3% at - 0.87 V vs RHE. The catalyst is found to be stable for 5 h of continuous operation and achieves a turnover frequency of 146.36 h^{-1}.

Keywords: *CO_2, electroreduction, bismuth oxychloride, formate, nitrogen doped carbon*

1. Introduction

There has been a growing interest to develop technologies for reducing CO_2 emissions in the atmosphere. Among various methods employed to tackle this challenge, electrochemical conversion of CO_2 to value added products has seen numerous development in the past decade [1-5], although the first work by Hori dates back to 1985 [6-8]. In the electrochemical reduction of CO_2 to value added products, electricity is used to form chemical bonds which is termed as electrocatalysis. A catalyst here plays a vital role not just by reducing the activation energy barrier of CO_2 electroreduction but by also affecting the selectivity, activity and stability of the reaction [9-11]. Most of the research has thus focused on the design of electrocatalytic materials for the selective conversion to various products such as CO, formic acid, methanol, ethanol, hydrocarbons and oxalic acid [12-20]. Majority of the studies have been done in aqueous electrolytes for producing products like carbon monoxide which is used in syngas, hydrocarbons such as methane and multicarbon products such as ethylene and ethanol [21,22]. The selectivity of a particular product from CO_2 reduction reaction has been found to depend not only on the catalyst employed but also on the electrolyte and reaction conditions such as temperature, pressure and pH of the electrolyte [23-25]. Among the various products that can be produced from CO_2, formic acid has wide industrial applications such as building blocks for fine chemicals and in fuel cells [26,27]. Hence, utilizing CO_2 to convert it into formic acid is a promising technology and ample research has been done to design suitable catalysts that can selectively convert CO_2 to formic acid.

In general, p-block metals such as tin (Sn), lead (Pb), indium (In) and bismuth (Bi) have been found to be efficient catalysts for the selective conversion of CO_2 to formate/formic acid [28]. An important factor here is to employ an electrocatalyst that can lower the overpotential of the CO_2 reduction reaction and suppress hydrogen evolution reaction (HER) which occurs in the same potential window. Bismuth and bismuth oxide in particular has been found to be efficient for the selective conversion to formate due to its high hydrogen overpotential and has found great interest as catalyst for CO_2 reduction in the past few years [29-33].

In the synthesis of such catalysts, numerous strategies have been employed to tune the structure, morphology and design catalysts that can satisfy the requirements of achieving high selectivity, efficiency and long term stability. Particularly interesting among those are metal single atom catalysts supported on low cost activated carbon black. The use of activated carbon black as support for these metal atoms is due to its high surface area and the presence of defects which enables a high adsorption capacity for metal cations in aqueous solution [34]. Methods such as nitrogen doping have also been employed for enhancing the dispersion of these metal atoms on carbon black [35]. Moreover, synthesis of catalysts supported on activated carbon black are effective for use in gas diffusion electrodes employing a membrane electrode assembly (MEA) where a carbon felt or carbon paper acts as the gas diffusion layer (GDL). In the methods employed for the synthesis of these catalysts, an aqueous solution of a metal salt is added to carbon black dispersed in water with vigorous stirring. Thereafter, a reducing agent such as $NaBH_4$ is added or annealing at elevated temperature is performed to obtain the catalyst.

In the present work, we report the synthesis of bismuth oxychloride dispersed on carbon (BiOCl-C) and nitrogen doped carbon (BiOCl-NC) using a facile ion adsorption process using bismuth acetate as precursor and discuss their catalytic activity for CO_2 reduction. Our studies reveal that bismuth oxychloride dispersed on nitrogen doped carbon show better catalytic performance than bismuth oxychloride supported on carbon for the selective conversion of CO_2 to formate and the catalyst was found to be stable during 5 hours of electrolysis. A faradaic efficiency of 84.3 % for formate was obtained for BiOCl-NC at -0.87 V vs RHE. To the best of our knowledge, this is the first study on the catalytic activity of bismuth oxychloride supported on nitrogen doped carbon for CO_2 electroreduction to formate.

2. Experimental

2.1 Catalyst preparation

Bismuth oxychloride supported on carbon black (BiOCl-C) was synthesized using commercially obtained Vulcan carbon and bismuth acetate. Briefly, 1g of Vulcan carbon was dispersed in 400 mL of Millipore water by sonicating it for 30 min. Bismuth acetate which is sparingly soluble in water was dissolved completely by adding 2g of bismuth acetate in 200 mL of 2 N HCl. This solution containing Bi^{3+} ions was added to the well dispersed carbon black suspension and stirred overnight for 12 hours (h) to adsorb Bi^{3+} onto carbon. The solution was then centrifuged and the obtained precipitate was dried at 60°C for 4 h. The dried powder was then annealed at 400 °C in a tubular furnace for 1 hour in an inert atmosphere obtained by flowing argon gas and BiOCl-C was obtained. To prepare bismuth oxychloride supported on nitrogen doped carbon (BiOCl-NC), a similar procedure was employed but before the annealing process, urea with a weight ratio of 10:1 to that of Bi^{3+}-C powder was taken, well mixed and annealed at 400°C to obtain BiOCl-NC. The schematic of this synthesis procedure is shown in Fig.1.

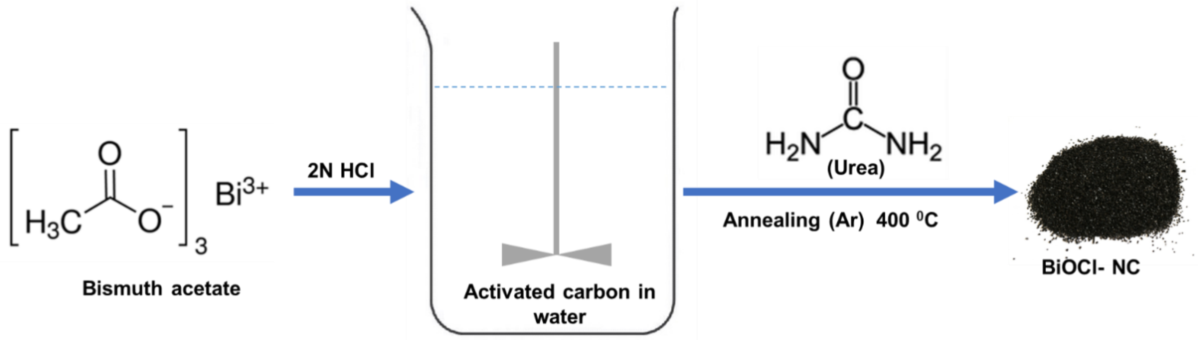

Fig.1. Schematic of the synthesis procedure for BiOCl-NC.

2.2 Electrochemical measurements

Electrochemical measurements were performed at room temperature using a Autolab Potentiostat in a three electrode cell configuration with a saturated calomel electrode (SCE) as the reference electrode and a Pt foil as counter electrode. A custom made two compartment gas tight H-cell made of Borosil glass was used for CO_2 reduction experiments. Nafion 117 was used as proton exchange membrane to separate the anode and cathode compartments.

FTO coated glass (Aldrich) was used as the working electrode. Catalyst ink was prepared by taking 15 mg of synthesized catalyst in 1 mL of isopropyl alcohol and adding 100 μL of 5% Nafion solution as binder. This mixture was sonicated for 30 min to obtain the catalyst ink. 80 μL of the prepared catalyst ink was dropcasted on FTO coated glass on a geometric surface area of 2 cm^2 to obtain a mass loading of 0.4 mg/cm^2. The resultant catalyst coated substrate was dried at 50° C for 4 h. Both anodic and cathodic compartments were filled with 30 mL of electrolyte solution (0.5 M $KHCO_3$). Before each electrolysis experiment, catholyte was saturated with CO_2 gas by continuously bubbling for 30 min. CO_2 bubbling was continued during electrolysis as well to ensure that sufficient reactant is present. The flow rate of CO_2 was fixed at 50 sccm at all times. Oxygen evolution was the major reaction occurring at Pt (counter electrode) in the anode compartment. Electrolysis was performed at various working electrode potentials and all potentials were converted to RHE using the following equation

$$E_{RHE}(V) = E_{SCE}(V) + 0.244\ V + (0.0591 * pH)$$

The pH of the CO_2 saturated electrolyte was found to be 6.7.

2.3 NMR detection of formate

CO_2 electroreduction experiments were performed for 3600 seconds and 1 mL of aliquots from catholyte was taken to detect the formation of formate by NMR spectroscopy. After each experiment, 0.3 mL of catholyte was mixed with 35 μL of 35 mM phenol which is used as internal standard for the quantification of formate. 0.2 mL D_2O was then added to this mixture. Solvent suppression was employed to reduce the intensity of water peak. The results were obtained using ^1H NMR scans (Bruker) and processed using MestReNova software. Formate was the only CO_2 electroreduction liquid product that was detected in the catholyte. Quantification of formate was done using calibration curve obtained by performing NMR scans of known concentration of formate using phenol as internal standard (See Fig. S1, Supporting Information).

2.4 Characterization of BiOCl catalysts

The surface morphologies of prepared catalysts were obtained by FESEM and TEM analysis. The crystalline nature of prepared BiO catalysts was studied using XRD. The oxidation states of Bi, O, Cl and N were studied using XPS analysis.

3. Results and Discussion

Fig.2 shows the linear sweep voltammograms (LSVs) of BiOCl-C and BiOCl-NC in CO_2 saturated 0.5 M $KHCO_3$ solution. It is clearly evident that BiOCl-NC exhibits current densities significantly higher than BiOCl-C implying better catalytic activity for CO_2 electroreduction.

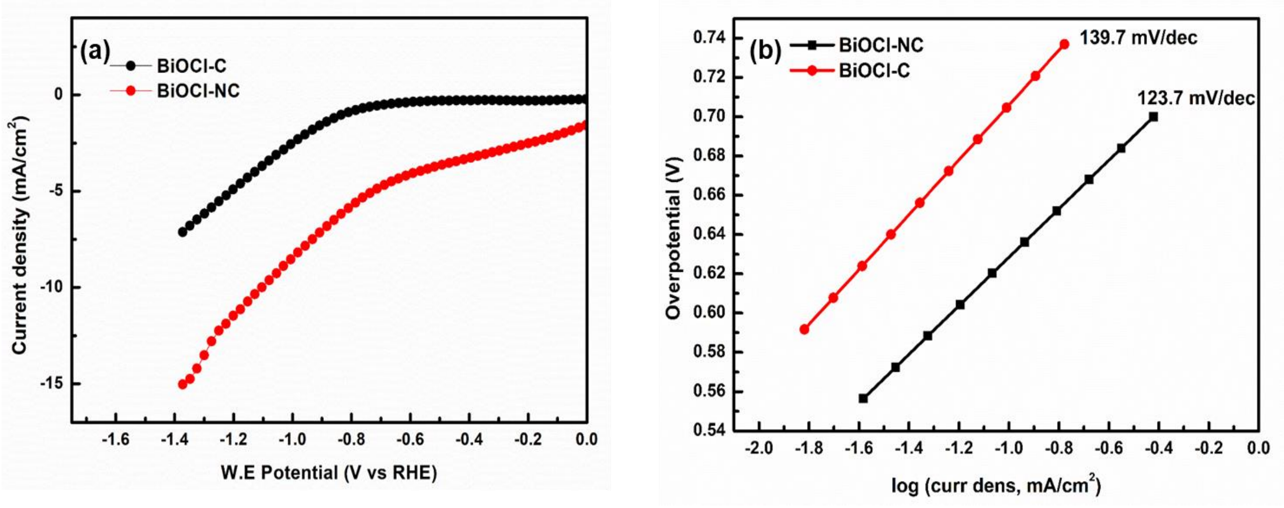

Fig. 2. (a)Linear sweep voltammograms (LSVs) of BiOCl-C and BiOCl-NC in CO_2 saturated 0.5M $KHCO_3$ solution at a scan rate of 50 mV/s. (b) Tafel slopes calculated for both the catalysts.

At a potential of -0.87 V vs RHE, a current density of 6.7 mA cm^{-2} was obtained in contrast to 1.3 mA/cm^2 for BiOCl-C. This is consistent with the Tafel slopes calculated which was 139.7 mV/dec for

BiOCl-C and 123.7 mV/dec for BiOCl-NC as shown in Fig. 2(b). The reduced tafel slope of 123.7 mV/dec for BiOCl-NC shows that BiOCl-NC exhibits a high intrinsic CO_2 reduction activity. It is plausible that this high catalytic activity is due to the enhanced dispersion of Bi atoms on carbon due to defects created by the doping of nitrogen. A tafel slope close to 118 mV/dec for both catalysts implies a similar mechanism of CO_2 reduction on both catalysts which is a one electron transfer to form CO_2^- intermediate on electrode surface. The transfer coefficient is hence close to 0.5 and the first reaction giving CO_2^- is the rate determining step [36,37].

Catalytic activity of support materials

In order to investigate if the support materials carbon (C) and nitrogen doped carbon (NC) had any effect on CO_2 electroreduction, linear sweep voltammetry (LSV) experiments were performed without dispersion of bismuth oxychloride atoms and the obtained LSV curves are shown in Fig. 3.

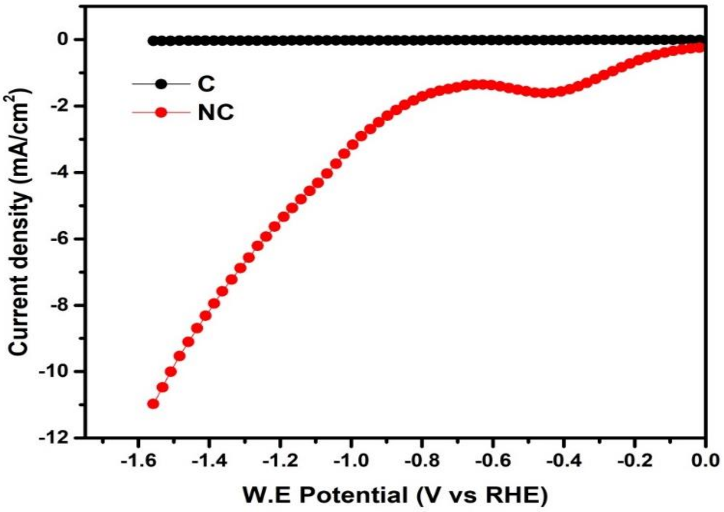

Fig. 3. Linear sweep voltammograms (LSVs) of carbon (C) and nitrogen doped carbon (NC) in CO_2 saturated 0.5 M $KHCO_3$ solution at a scan rate of 50 mV/s.

It is evident from these results that the carbon black had no catalytic activity showing zero current density at the applied potentials. Nitrogen doped (NC) carbon exhibited a current density of -2.8 mA/cm^2 at a potential of -0.87 V vs RHE, which is significantly less than that of BiOCl-NC. Although NC shows catalytic activity, the faradaic efficiency of formate produced was only 16.5% (See Fig. S3). This is in accordance with some of the previous studies, which reported that NC has a higher selectivity for carbon monoxide than formate [38-40]. So, we suspect that NC has a higher selectivity for CO or other gaseous products which we could not estimate due to the unavailability of gas chromatography.

In order to further investigate the catalytic activities of the catalysts, electrochemical impedance spectroscopy (EIS) was performed in CO_2 saturated 0.5 M $KHCO_3$ electrolyte solution. This is important to evaluate the kinetic behaviour of the BiOCl-C and BiOCl-NC electrodes. EIS measurements were performed with respect to open circuit potential at frequencies ranging from 100 KHz to 100 mHz and the Nyquist plots obtained are shown in Fig.4. The inset in Fig. 4 is the equivalent circuit-fit for the electrochemical systems which helps to explain the physical parameters. The R_s represents the body impedance of the substrate electrode, the catalyst and the impedance resulting from the electrolyte solution. It is worthwhile to note that since the electrode is in contact with the electrolyte solution, the change i.e. the reduction of R_s from 33.02 to 29.64 ohm.cm^2 is apparently due to the introduction of BiOCl-NC catalyst which shows more conductivity.

The R_{ct} represents the charge transfer resistance, which indicates the resistance towards the kinetic reaction in the electrocatalytic process. Nyquist plots clearly show the enhanced catalytic activity of BiOCl-NC due to its low charge transfer resistance compared to BiOCl-C. This means that the interfacial electron transfer rate has increased in the CO_2 reduction reaction using BiOCl-NC (See Table 1). Hence the hydrated CO_2 molecules easily react with electrons from the BiOCl-NC electrodes to form a CO_2^{*-} radical intermediate. These findings are supported by the lower arc radius of BiOCl-NC in the Nyquist plot which further shows that the charge transfer resistance for CO_2 electroreduction is significantly less for BiOCl-NC than BiOCl-C.

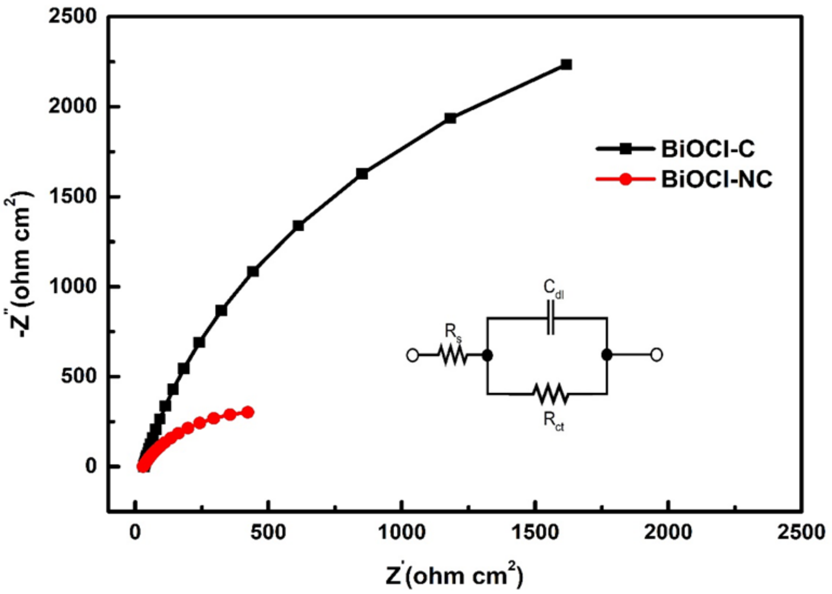

Fig. 4. Nyquist plots of BiOCl-C and BiOCl-NC obtained by EIS with respect to OCP.

Table 1: R_s and R_{ct} values of BiOCl-C and BiOCl-NC used in electroreduction of CO_2 to formate

Catalyst	**R_s (ohm.cm^2)**	**R_{ct} (ohm.cm^2)**	**C_{dl} (F. cm^2)**
BiOCl-C	33.02	6388	4.566×10^{-4}
BiOCl-NC	29.64	910.2	18.86×10^{-4}

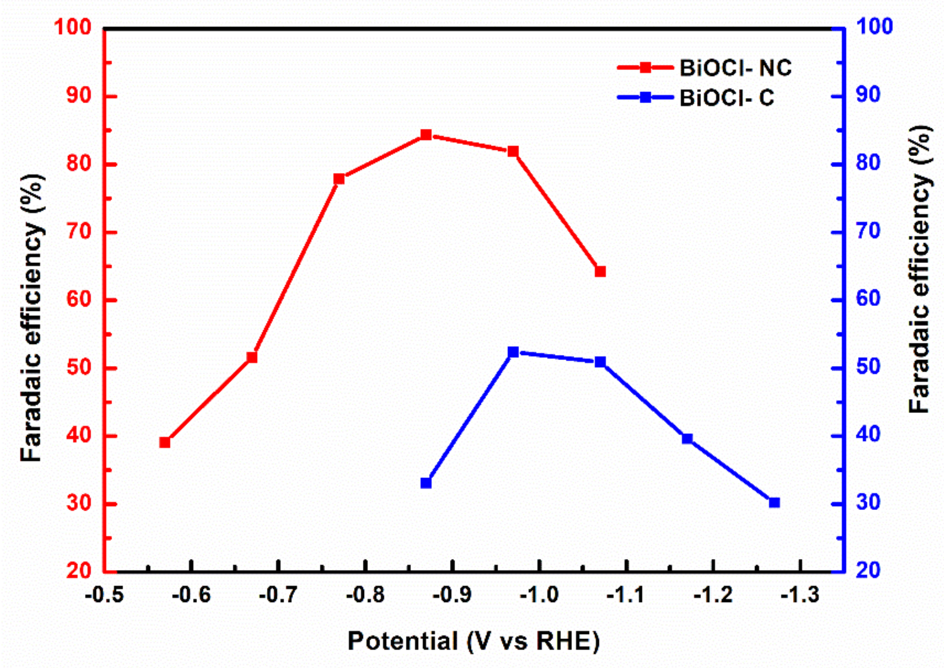

Fig 5. Faradaic efficiency for the electroreduction of CO_2 to formate at different potentials for BiOCl-C and BiOCl-NC.

The faradaic efficiency (F.E) of formate obtained at various potentials for both catalysts is shown in Fig. 5. The F.E increases with increasing potentials upto a potential of -0.87 vs RHE for both catalysts. Thereafter, formate production starts to decrease indicating the increase in hydrogen evolution reaction and subsequent decrease at higher potentials. The equations for the F.E calculation are shown in equation 2 (Supporting Information).

Morphological study of the catalyst

Fig. 6(a) and (b) shows the FESEM images of BiOCl-C and BiOCl-NC which clearly indicate the sheet structure of bismuth atoms. In Fig 6 (c) and (d) a uniform dispersion of atoms of BiOCl is seen which is possibly due to the enhanced dispersion of atoms on nitrogen doped carbon.

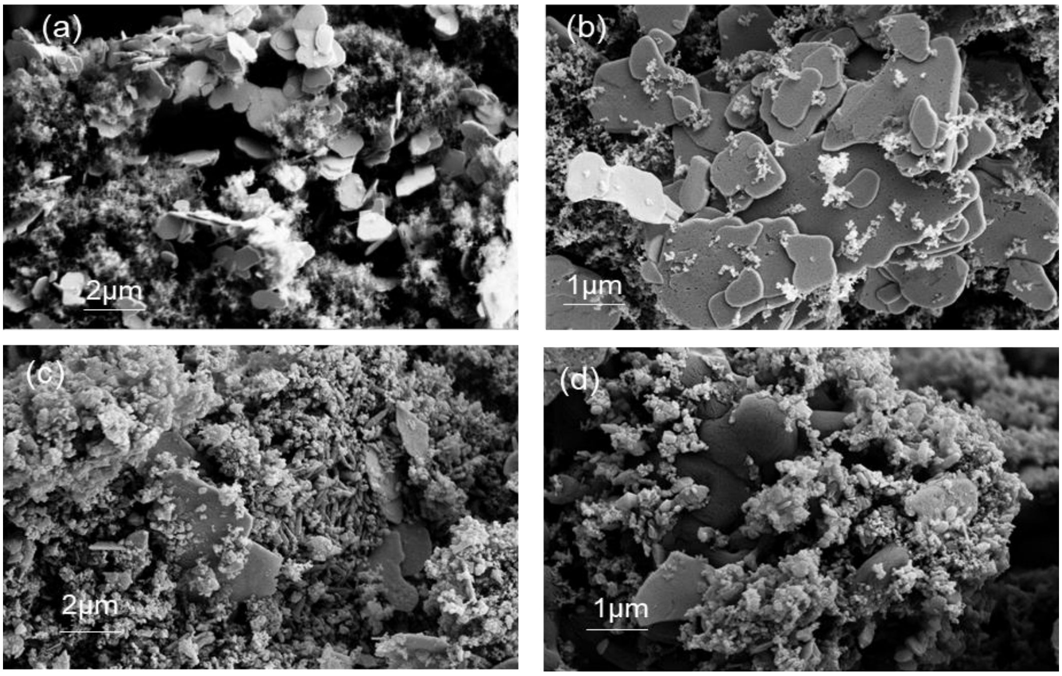

Fig. 6. FESEM images of (a) and (b) BiOCl-C, and (c) and (d) BiOCl-NC showing the sheet structure of bismuth atoms.

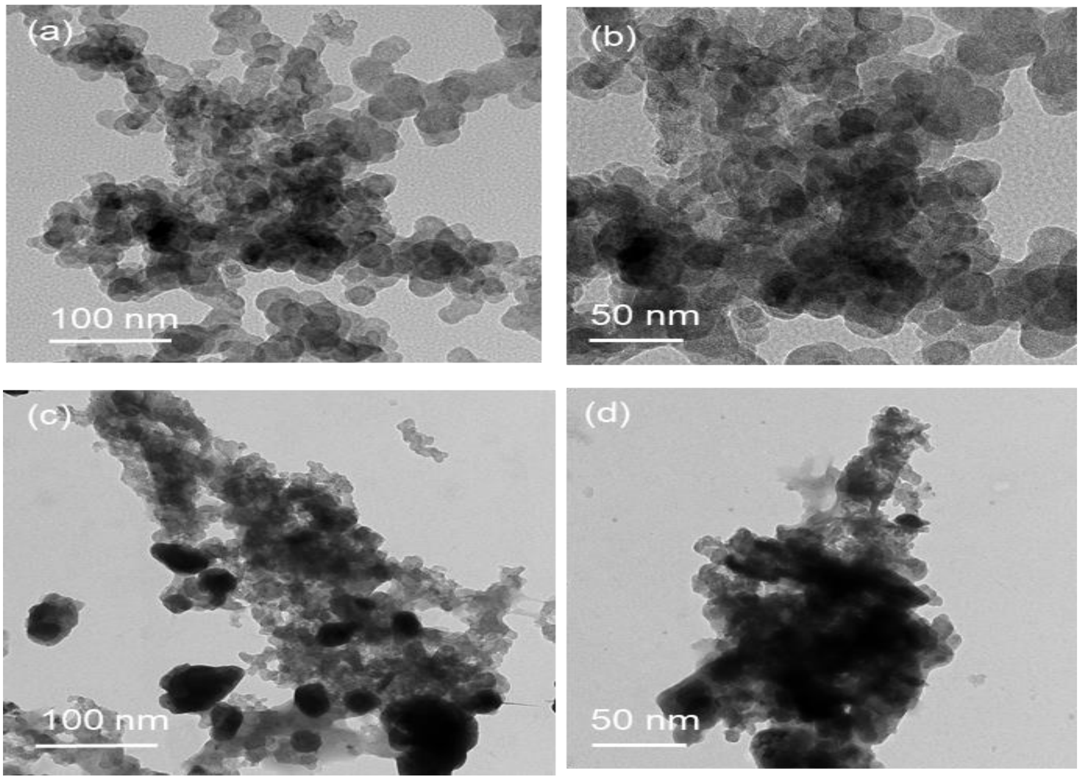

Fig.7. HRTEM images of (a), (b) BiOCl-C and (c), (d) BiOCl-NC showing the dispersion of bismuth atoms on the surface of activated carbon.

This was also evident from the HREM images shown in Fig.7 where an enhanced and uniform dispersion of bismuth atoms on nitrogen doped carbon are evident. Both catalysts clearly show the bismuth oxychloride atoms located on the surface of activated carbon. In addition, XPS results also confirmed the enhanced dispersion of Bi atoms on NC compared to that of carbon support alone. The atomic concentrations of Bi was 2.23 at % in BiOCl-NC in contrast to 1.14 at % for BiOCl-C clearly confirming the enhanced dispersion of BiOCl in nitrogen doped carbon.

XRD and XPS analysis

X-ray diffraction patterns of catalysts were acquired before and after the CO_2 electroreduction experiments. Diffraction peaks of both catalysts before electrolysis matched well with the values reported in literature (JCPDS 06-0249) confirming the tetragonal structure of BiOCl [41]. After electrolysis for 1 hour, all the diffraction peaks were present however the intensity of peaks decreased as shown in Fig.8(b). Similarly, for BiOCl-NC only few differences in diffraction peaks was observed indicating good stability of the catalyst for CO_2 electroreduction. (See Fig.8 (d)). This difference is probably due to the reduction of BiOCl (Bi^{3+}) to metallic bismuth (Bi^0) after the reduction reaction as reported earlier where it was also found that leached Cl^- ions had no influence on the performance [42]. It is thus clearly evident that the Bi (001) facets present in BiOCl is responsible for the reduction of CO_2 to formate. In the addition, there is a minor transformation that actually emphasizes the reduction of Bi^{3+} to Bi^{o}, which is in line with the XPS analysis below and a literature report. A critical look at the peak at $2\theta = 28^0$ shows an increase in the major peak's intensity due to increased pure Bi^{o} formation. The peak due to Bi^{o} has been reported by Peng et al. [43], which confirms the increase in the intensity of the peak at $2\theta = 28^0$ as due to minor transformation of Bi^{3+} to Bi^{o}. The observed shift could also be due to the same reason. But overall, it does not affect the catalytic property significantly.

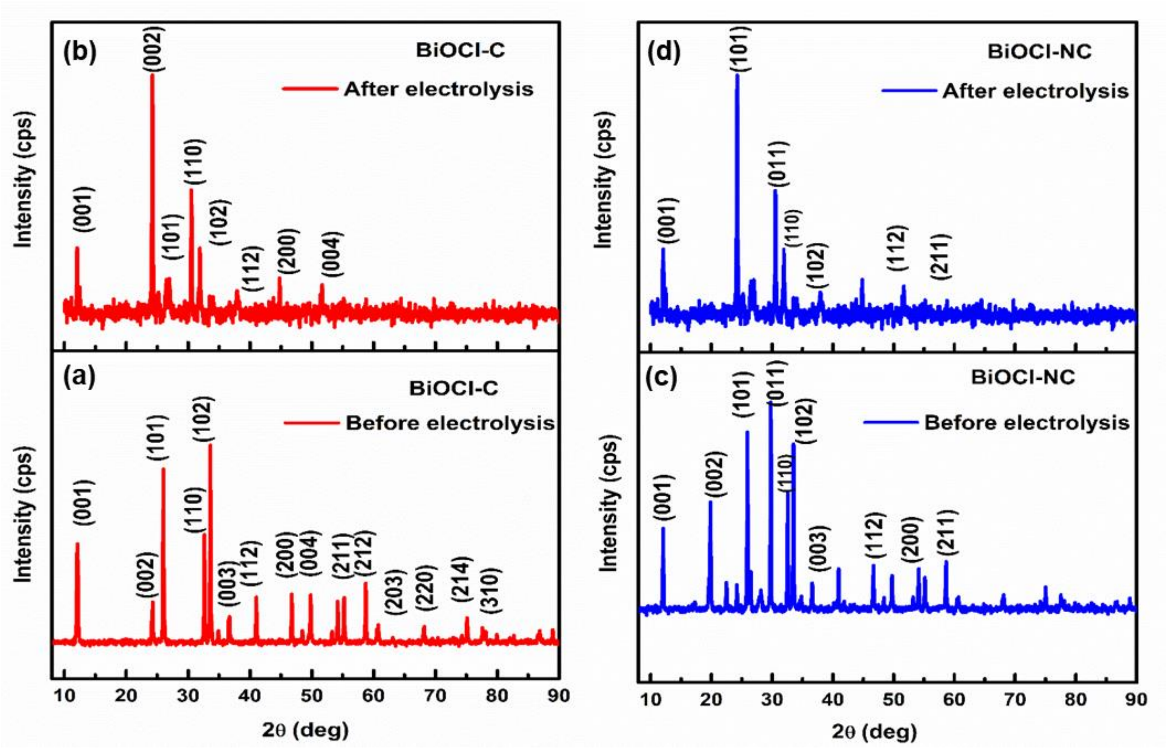

Fig 8. X- ray diffraction patterns of BiOCl-C (a) before and (b) after electrolysis and BiOCl- NC (c) before and (d) after electrolysis performed at -0.87 V vs RHE.

Since, BiOCl-NC clearly show better catalytic activity for CO_2 electroreduction to formate we focus our further discussion on the catalytic performance of BiOCl-NC.

In order to further elucidate the surface composition and chemical states of elements present in the BiOCl-NC, XPS measurements were conducted. The high resolution XPS spectra of Bi 4f, O 1s, Cl 2p and total survey spectra are shown in Fig 9. The two strong peaks at 158.7 eV and 164.0 eV can be assigned to the 4f (7/2) and 4f (5/2) whereas the strong peaks at 530.9 eV, 197.4 eV and 198.9 eV correspond to O 1s, Cl 2p (3/2) and Cl 2p (1/2) respectively. As mentioned earlier, some of the previous studies using bismuth oxyhalides as catalyst for CO_2 reduction have reported the reduction of bismuth oxyhalide to metallic bismuth upon electrolysis. To investigate this, the high resolution XPS spectra of BiOCl-NC was acquired after electrolysis for 1 h and the obtained spectra is shown in Fig.10.

It can be seen that two strong peaks at 158.2 and 163.6 eV are observed corresponding to Bi 4f (7/2) and Bi 4f (5/2) of BiOCl-NC. Interestingly, in addition to these peaks, two small peaks at 156.2 eV and 161.3 eV are observed and this is essentially due to the formation of metallic bismuth. The presence of these two peaks with lower binding energy values confirms the partial reduction of bismuth oxychloride (Bi^{3+}) to metallic bismuth (Bi^0) and is in accordance with some of the previous reports [43].

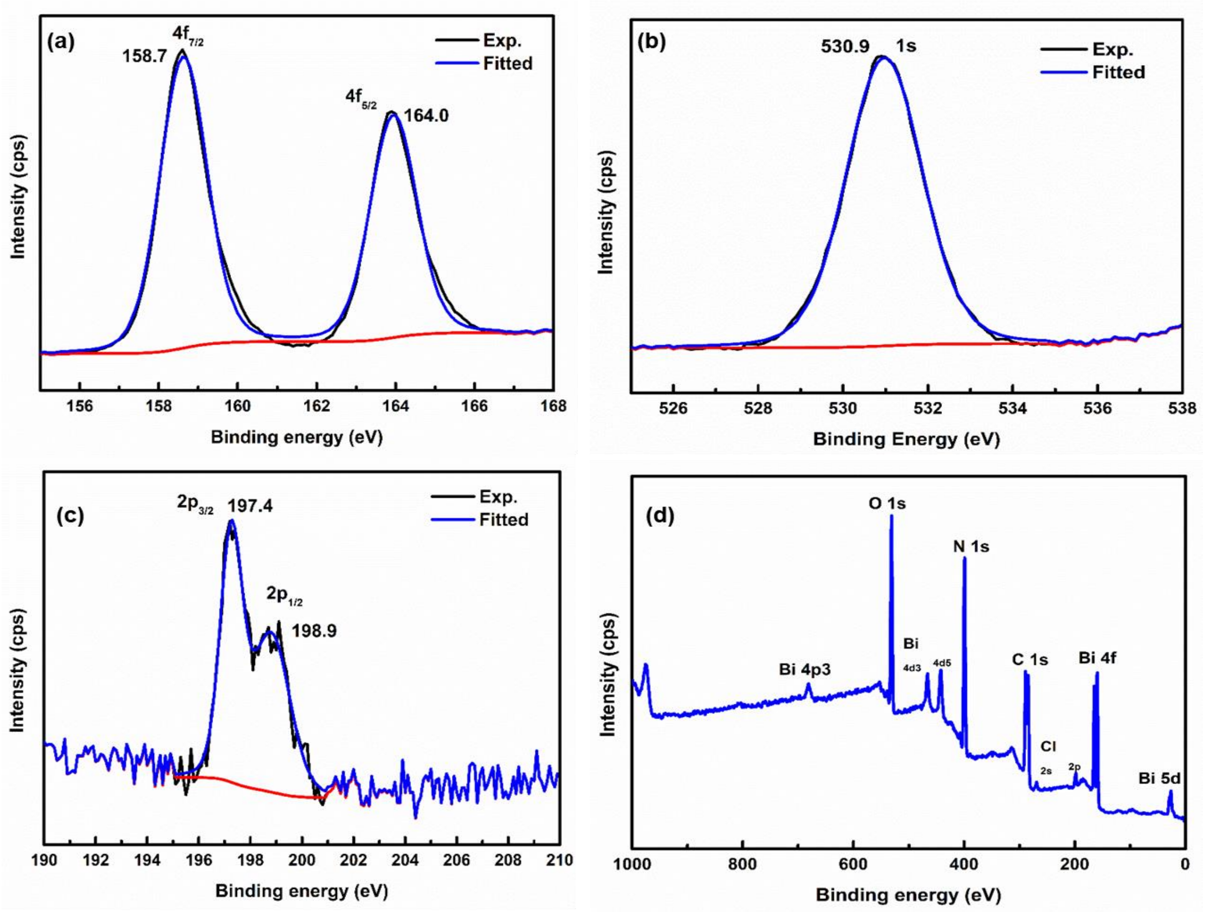

Fig. 9. XPS spectra of BiOCl-NC;(a) Bi 4f region, (b) O 1s region and (c) Cl 2p region and (d) survey pattern of the sample.

It has to be emphasized here that complete reduction of BiOCl to Bi does not take place as the presence of chlorine and oxygen is observed even after one hour of electrolysis. Also, this reduction from Bi^{3+} to Bi does not have any significant impact on the electroreduction of CO_2 to formate which is discussed later in the stability of catalyst section.

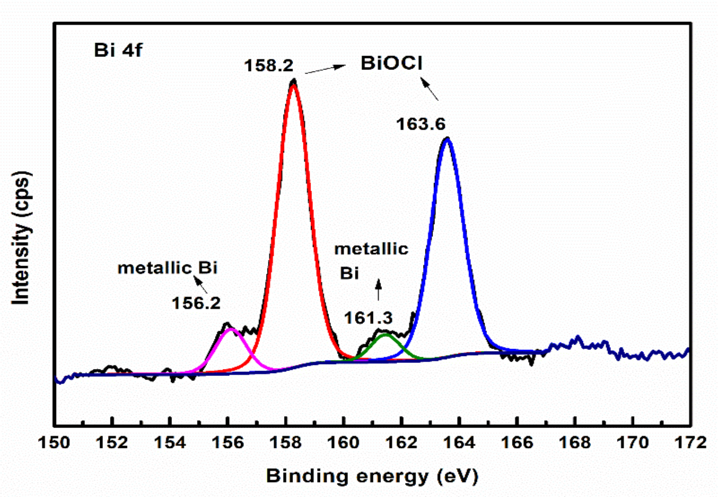

Fig. 10. High resolution XPS spectra of BiOCl-NC after 1 h of electrolysis.

In order to further understand if the transformation of BiOCl to metallic bismuth has occurred, XPS analysis was done on the sample after 5 h of electrolysis and the high resolution Bi peaks are as shown in Fig. 11. It can be observed that there are two peaks at 156.2 and 161.8 eV which can be assigned to the 4f (7/2) and 4f (5/2) of BiOCl-NC. No other peaks were observed and this reduction in the binding energy from 158.2 eV to 156.2 eV and 163.6 eV to 161.8 eV clearly confirms the complete transformation to metallic Bi.

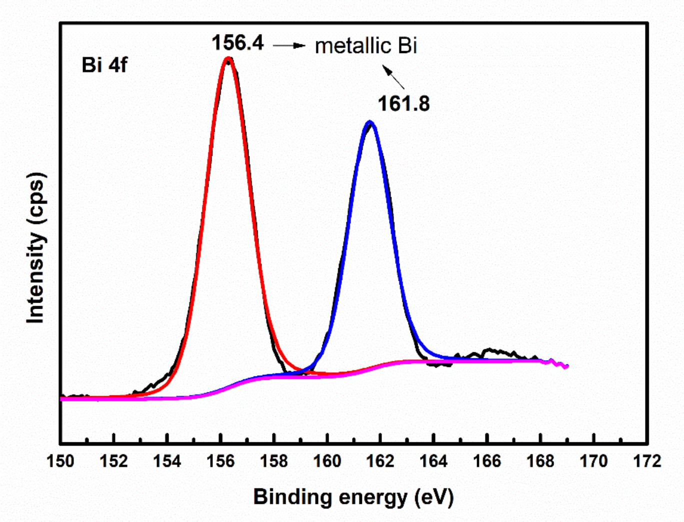

Fig. 11: High resolution XPS spectra of BiOCl-NC after 5 h of electrolysis.

Evaluation of Turnover frequency

In order to understand the efficiency of the catalyst, turnover frequency (TOF) for the CO_2 reduction reaction to $HCOO^-$ was calculated based on the 2 electron pathway. Here, 15 mg of catalyst was mixed with 1mL isopropanol and 100 µL of Nafion solution on 2 cm^2 area of FTO glass yielding a mass loading of 6.5 mg/cm^2. The content of Bi in the catalyst measured from XPS is 2.23 wt%. The turnover frequency is given by,

$$TOF = \frac{Turnover\ no.for\ HCOO^-/geometric\ area}{No.of\ active\ sites/geometric\ area}$$

The turnover number for HCOO$^-$ is given by,

$$TON = \frac{J \times t \times F.E_{HCOO^-}}{2F} = \frac{6.5 \times 10^{-3} \times 3600 \times 0.843}{2 \times 96485} \times 6.02 \times 10^{23}$$

$$= 6.156 \times 10^{19} cm^{-2} h^{-1}$$

The number of active sites per cm^2 is given by,

$$N = 6.02 \times 10^{23} \times (\frac{Wt.of\ Bi\ on\ electrode}{Mol.wt\ of\ Bi})$$

$$= 6.02 \times 10^{23} \times (\frac{6.5 \times 10^{-3} \times 2.23 \times 10^{-2}}{208})$$

$$= 6.02 \times 10^{23} \times 6.987 \times 10^{-7} cm^{-2}$$

$$N = 4.206 \times 10^{17} cm^{-2}$$

So,

$$TOF = \frac{6.156 \times 10^{19}}{4.206 \times 10^{17}} = 146.362\ h^{-1}$$

Hence, the turnover frequency is 146.362 h^{-1} where the current density for CO_2 reduction reaction is 6.5 mA/cm^2 with a F.E (HCOO$^-$) of 84.3 %.

Stability of catalyst

Beyond the electrocatalytic activity, an important criterion for practical utilization is the durability of the catalyst. To investigate this, electrolysis at a constant potential of -0.87 V vs RHE (choronoamperometry) was performed and the catalyst was found to be stable for 5 h with no significant change in the current density (See Fig.11). The faradaic efficiency (F.E) of formate after 5 h of electrolysis was calculated be to be 78.3 % (Fig. S2). This slight decrease in F.E of formate from 84.3% after 1 h to 78.3% after 5 h is possibly due to an increase in H_2 evolution after 5 hours. Further, a slight increase in partial current density is evident (Fig.11) during the first 1 h of electrolysis which is essentially due to the transformation of BiOCl to Bi. This is also clearly observed from XPS spectra after 1 hour of electrolysis (Fig 10). One of the previous studies by Liu et.al also found that the transformation to metallic Bi results in an increase in current density where bismuth oxyiodide was used as the catalyst [44].

In contrast to the presence of both BiOCl and Bi atoms after 1 h of electrolysis, they had reported the complete transformation of Bi $^{3+}$ to Bi^{0} after 1 h of electrolysis. This is possibly because of their electrolysis experiment being performed at higher current densities resulting in the faster reduction to metallic bismuth.

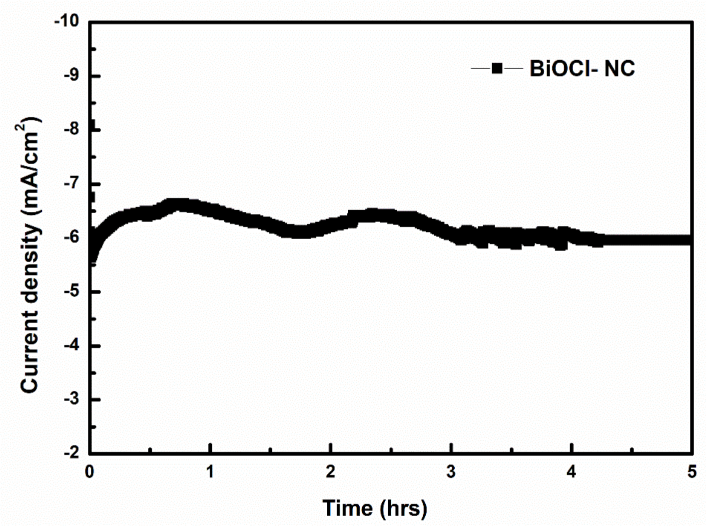

Fig. 11. Stability test for CO_2 electroreduction to formate using BiOCl-NC performed at a constant potential of -0.87 V vs RHE.

It has to be noted here that although the transformation of bismuth oxychloride to metallic bismuth occurs, no significant decay in current density is observed for 5 h of electrolysis. This confirms that this transformation does not affect the performance of electroreduction of CO_2 to formate and the presence of Bi (001) facets is responsible for this electrochemical reduction to occur.

4. Conclusion

In conclusion, bismuth oxychloride dispersed on nitrogen doped carbon was found to be an efficient catalyst for the electroreduction of CO_2 to formate with high selectivity and activity. A maximum faradaic efficiency of 84.3 % towards formate was produced and the catalyst remaining relatively stable for 5 h of electrolysis. Synthesis of catalyst supported on carbon using bismuth acetate, HCl and urea as precursors and subsequent annealing at 400^{0} C is a facile, efficient and scalable process. Nitrogen doping enhances the dispersion of BiOCl atoms on the carbon support enhancing its catalytic activity towards CO_2 reduction to formate. Although, nitrogen doped carbon without any BiOCl dispersion showed some catalytic activity towards CO_2 reduction, the faradaic efficiency of formate produced is only about 16.5% showing its poor selectivity towards formate production. Although the current densities obtained for CO_2 electroreduction are relatively low, the use of flow cell and gas diffusion electrodes (GDE) will provide a better performance and will be the focus of our future studies. Nevertheless, this facile synthesis procedure and catalytic performance of BiOCl-NC catalyst in H-cell opens up avenue for scaling up highly selective CO_2 reduction using flow cell reactors and GDE.

Acknowledgement

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Conflicts of Interest

There are no potential conflicts of interest reported by the authors.

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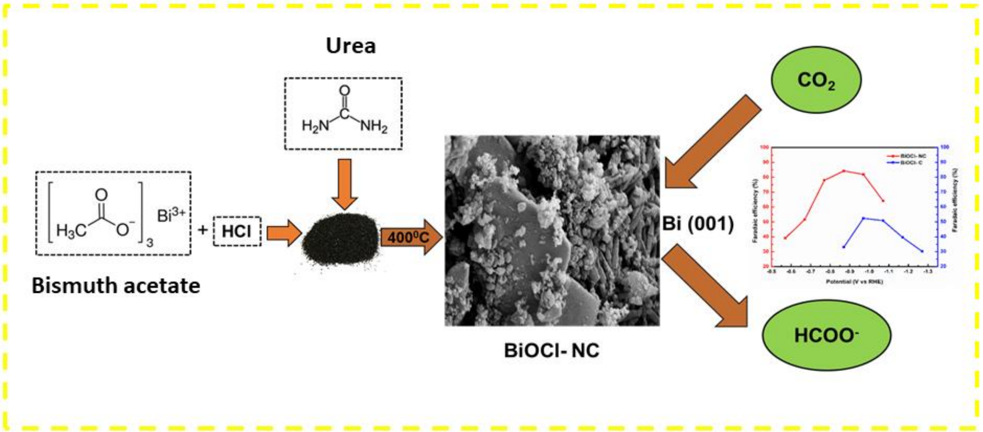

Bismuth oxychloride supported on nitrogen doped carbon synthesized by a facile ion adsorption process using bismuth acetate and urea as precursors. It is found to be a good electrocatalyst for the electrochemical reduction of CO_2 to formate in 0.5 M $KHCO_3$ solution.