Synthesis and characterisation of monometallic metal oxide on graphene support: electrocatalyst for carbon dioxide conversion

Thesis

Submitted for the fulfilment of the Degree

of

Master of Science

By

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CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis and characterisation of monometallic metal oxide on graphene support electrocatalysts for carbon dioxide conversion"** being submitted by Mr. Kartik Sharma to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala in partial fulfilment of the requirements for the award of degree of **Master of Science in Chemistry,**is an authentic record of bonafide work carried out by him under our guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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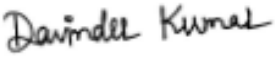

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ABSTRACT

Carbon dioxide is the major greenhouse gas and due to the reckless use and burning of fossil fuels by human beings its level is increasing in the atmosphere. As a result of which, it is causing problems like global warming to the planet. Therefore the increasing levels of carbon dioxide must be controlled or better reverted to avoid undesirable climate change. There are several ways to mitigate this problem of enhancement in carbon dioxide level. Among these, carbon dioxide capture and sequestration (CCS) is in use from last two decades. Carbon dioxide capturing can be done at three stages, Pre-combustion, oxyfuel combustion and post combustion. The drawbacks associated with this method are, high cost of CO_2 capture and transport and lack of industrial commitments and incentives, it also damages the environment due to accidental leakage of CO_2 from the pipelines or storage reservoir. CO_2 utilization is another technique, in which atmospheric CO_2 can be converted to useful chemicals and renewable fuels. This technique will not only reduce the CO_2 level in atmosphere but also it will provide valuable products leaving behind the drawbacks associated with CCS technique. Many CO_2 utilization techniques are popular, this includes the reduction of CO_2 by chemical, photochemical, radiochemical and electrochemical methods.

Different studies and experiments reveal that among them the process of electrochemical reduction is most promising and efficient method, because of its simplicity, small chemical intake and environment friendly nature. Due to the stable nature of CO_2, it is often challenging to reduce it in different products. Other than this, there are some shortcomings like hydrogen evolution reactions (HER) and formation of multiple products that arise during the electroreduction process; therefore it is essential to get a suitable electrocatalyst which can produce the reduction products selectively with high faradic efficiency.

Previous studies, reveals that Cu based electrocatalysts are most effective for CO2, electrochemical reduction process due to their excellent catalytic activity, high faradic efficiency and good stability. In the present work, synthesis of monometallic metal oxide (Cu_2O) on graphene supported electrocatalyst has been done and these are further characterised with the help of suitable techniques like XPS, Raman spectroscopy and FE-SEM. On the basis of characterisation results, prepared catalyst was found suitable to be used as electrocatalyst for CO_2 reduction to produce alcohols.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

V: Volt

^{o}C: Degree Celsius

ABBREVIATIONS

CO_2	Carbon dioxide
GO	Graphene oxide
Cu_2O	Cupric oxide
CuO	Copper oxide
$CuCl_2$	Cuprous chloride
GN	Graphene
NaOH	Sodium hydroxide
$NH_4OH.HCl$	Hydroxyl ammonium chloride
XRD	X-ray diffraction
LSV	Linear Sweep Voltametery
F.E.	Faradic Efficiency
ESCA	Electron spectroscopy for chemical analysis
FESEM	Field emission scanning electron microscope
Conc.	Concentrated
NGQDs	N-doped graphene quantum dots
HER	Hydrogen evolution reaction
SHE	Standard Hydrogen electrode
STM	Scanning tunnelling microsocpe
GDE	Gas diffusion electrode

CODH	Carbon monoxide dehydrogenase
CCS	Carbon dioxide capture and sequestration

Chapter 1

INTRODUCTION

Overview

This chapter deals with various greenhouse gases especially CO_2. It discusses the major concern of rise in level of CO_2 and the adverse effects caused by it. Various methods like CCS and CO_2 utilisation have been discussed here to combat the problem of CO_2. Due to the simplicity and environment friendly nature of electroreduction, major emphasis has been shown on the electroreduction of CO_2 to various products and the type of electrocatalysts required for the electroreduction have also been discussed in this chapter.

1.1 Background

Carbon is the most essential element present on earth. It is present in rocks, air and oceans. Every living being is made up of carbon. In atmosphere it is found in combined form with oxygen in the form of carbon dioxide. Carbon dioxide is a linear and centrosymmetric molecule in which carbon atom is covalently double bonded to two oxygen atoms. It is an important gas present in atmosphere. It is the major component of carbon cycle in which carbon dioxide is exchanged between Earth's oceans, rocks and biosphere. The level of carbon dioxide present in atmosphere is around 0.03%, numerically it accounts for very small fraction but this amount is making a huge impact on the daily life of organisms. It is released into the atmosphere by both natural and human resources. Natural sources include decomposition, ocean release and respiration. Human sources come from activities like industrial production, deforestation as well as the burning of fossil fuels like coal, oil and natural gas. Industries contribute to about 36% of carbon dioxide emission in atmosphere and these are mainly from large manufacturing industries. The industries like cement, chemical, petrochemical and iron account for more than two third of this amount. Therefore due to human sources the level of carbon dioxide is increasing at enormous level day by day. This rise in level of carbon dioxide is causing an increase in greenhouse effect, due which more heat is captured by the atmosphere of earth as a result of which the planet becomes warmer than it usually is and this phenomenon is called as global warming.

1.2 Effects of Carbon Dioxide

The rise in the level of greenhouse gases is measured as the main reason for global warming. The main greenhouse gases are carbon dioxide, ozone, methane, nitrous oxide and CFC's and among them carbon dioxide is the chief gas which contributes to greenhouse effect largely. Carbon dioxide is the main pollutant that warms our planet earth. It is one of the most notorious gas which is responsible for the global warming[1]. The concentration of carbon dioxide increases around 3.9% per year. Figure1.1 shows the rise in level of carbon dioxide in recent years. Therefore the ever increasing levels of carbon dioxide are contributing more towards the menace of global warming with each year. The earth's temperature is increasing day by day due to the burning of fossil fuels which emits CO_2 at vast level. This increase of CO_2 in surrounding further thickens the greenhouse blanket which traps the heat. In recent years the level of carbon dioxide has increased enormously which has caused a lot of problems like melting of polar ice caps as a result of which the global sea level has increased upto large levels. Moreover marine life also gets affected by the rise in carbon dioxide levels in the oceans which drops the pH and further increase the acidity of the ocean water thus making it unsuitable for the marine animals to live in it.

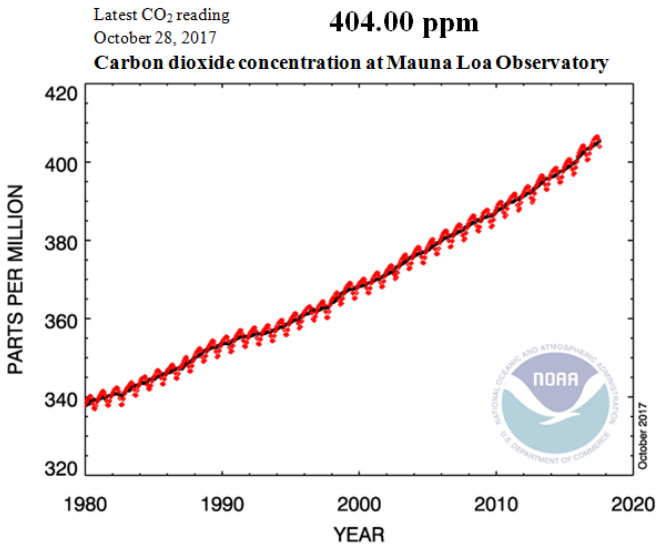

Figure1.1 Graph showing the increasing carbon dioxide levels in recent years

[Source: NOAA].

1.3 Methods to combat the problem of Carbon dioxide

The emission of carbon dioxide needs to be reduced drastically to overcome the unpleasant effects leading to climate change and global warming. There are some approaches to overcome this and these are:

- Switch to renewable sources of energy like wind, solar and water from fossil fuels.
- Increased use of the fuels like hydrogen, natural gas etc (low carbon fuels).
- Capture the carbon dioxide and convert the captured carbon dioxide to convenient commercial and liquid fuels.
- Carbon dioxide utilisation.

  However, the first method mentioned is not as beneficial as the other one because amount of energy acquired from the renewable sources is limited to just 30% because of their intermittent nature. Thus in order to obtain full benefits we mostly switch to the other methods. In order to mitigate the problem of global warming carbon dioxide capturing is the pathway that is usually done to prevent the release of carbon dioxide into the atmosphere. There are generally three main processes through which carbon dioxide capture is done and these are pre combustion capture, oxyfuel combustion capture and post combustion capture. And the detailed schematic diagrams of all of them are given below.

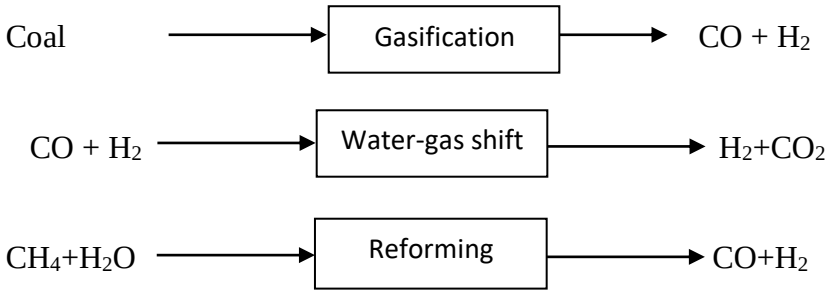

Figure1.2: Schematic diagram of pre-combustion CO_2 capture process

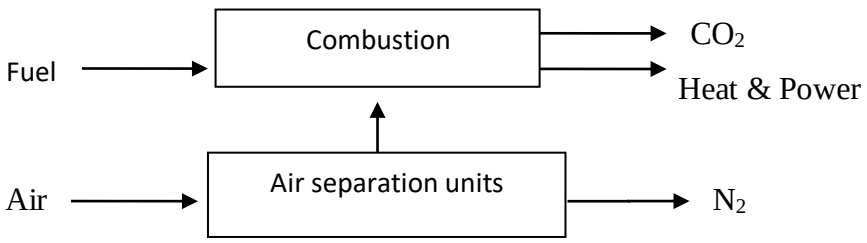

Figure1.3: Schematic diagram of oxyfuel CO_2 capture process

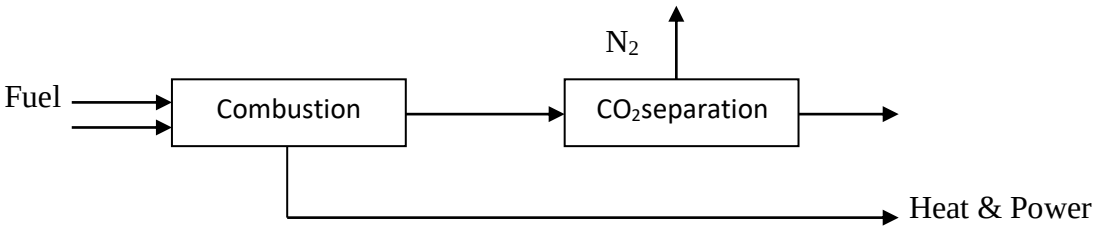

Figure1.4: Schematic diagram of post combustion CO_2 capture process

Despite being productive there are some barriers that are hindering the practical applications of carbon dioxide capture and they include (1) high cost of CO_2 capture, separation and transportation to user sites (2) Limited market size and investment incentives (3) Lack of industrial commitments for enhancing CO_2 based chemicals.

1.4 Carbon dioxide utilisation

Carbon dioxide utilisation generally converts carbon dioxide into commercially useful products. There are several ways through which carbon dioxide is being utilised and is changed into different products. Carbon dioxide reduction is the foremost technique that is used. Different methods such as: chemical, radiochemical, electrochemical and photochemical methods of reduction have been done for the conversion of carbon dioxide. In nature reduction of carbon dioxide is carried with the help of (chemicals) enzymes mainly CODH present in several bacteria. Two major classes of CODH have been identified. CODH containing a Mo-[2Fe-2S]-FAD active sites has been found in aerobic bacteria whereas a different class having Ni-[3Fe-4S] CODH enzymes have been found in anaerobic bacteria. Both the classes containing the metal centres catalyse the conversion of carbon dioxide. They reduce carbon dioxide to methane by undergoing various reductive pathways. Photochemical reduction uses sun's energy for reduction of carbon dioxide whereas the radiochemical reduction makes the use of radioactive elements for the process of reduction. The electrochemical reduction of CO_2 makes the use of CO_2 and H_2O as reactants and the process is carried out in electrolytic cell.

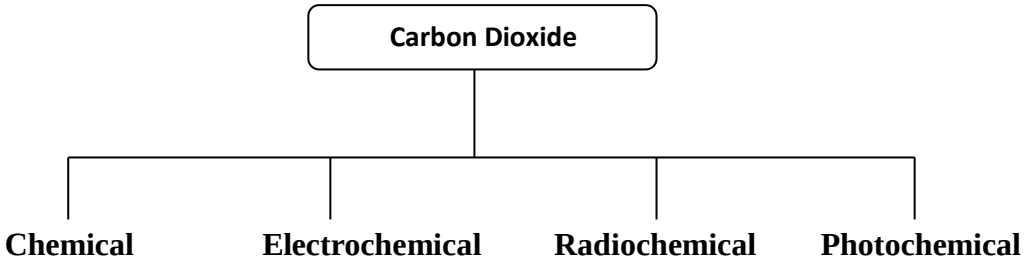

Figure1.5: Different routes of carbon dioxide reduction

1.5 Electroreduction

However different experiments and studies reveal that the electrochemical or so called as electrochemical reduction method is the most efficient and promising method for carbon dioxide conversion[2] and it is because of the following reasons:

- Electrochemical method of conversion is controllable directly by adjustment of electrode potential that is applied.
- In this method the reaction can be driven by the electricity that is generated renewably and that further helps to store irregular , non dispatchable renewable sources such as wind in the type of bonds that are mostly chemical.
- Electrochemical system have a footprint that is small, moreover it requires small chemical intake and operates at room temperature.
- Its simplicity and environment friendly nature makes it the best suited method.

In reduction of CO_2 electrochemically the first and foremost step is the activation of stable molecule of CO_2. As the C atom has double covalent bonds with oxygen and the two pairs of electrons are shared between the atoms. As the carbon dioxide has linear sp hybridised structure therefore as a result of which the bond energy is very high (~532KJ.mol) thus making it stable. Therefore appropriate electrical potential is needed for the activation of CO_2.Moreover the activation of CO_2 requires the change in its geometry from the linear structure to the bent CO_2 anion radical, which further results in a very slow self exchange rate for the CO_2/.CO_2^- couple, thus making it rate determining step. This is the most energy exhaustive step in electro reduction and requires -1.9V vs SHE. Therefore efficient electrocatalysts are needed to reduce the activation energy barrier. Despite being so fruitful there are some disadvantages of electrochemical reduction and that is the HER reaction at cathode, and this mainly occurs due to similar reduction potentials of CO_2 and H_2.This leads to competition between the HER and

electrochemical reduction of carbon dioxide during the whole process which results in significant consumption of supplied energy for HER rather getting used up in reduction of CO_2.As a result of which the current efficiency of electrochemical reduction is adversely affected. Therefore suitable electrocatalysts are required to increase the selectivity of reaction towards electrochemical reduction.

1.6 Electrocatalysts

A catalyst is a substance which increases the rate of reaction without participating in it and an electrocatalyst does the electron transfer and changes the kinetics of reaction. Apart from this, electrocatalysis differs from usual catalysis as, in electrochemistry, the reaction rate depends not only on given system parameters (composition of the catalyst and electrolyte, temperature, state of the catalytic electrode surface), but also on the electrode potential. Thus, in a given system, the potential can be varied by a few tenths of a volt; while as a result, the reaction rate will change by several orders of magnitude. Electrocatalysts are also interesting because in electrochemical reactions, the catalyst surface is not only in contact with the reacting species but also with other species like electrolyte ions and solvent which in turn manipulate the properties of the surface and give rise to special reaction features. The electrochemical reduction of CO_2 is usually promoted by the use of electrocatalysts.

1.7 Types of electrocatalyts

Electrocatalyts can be either homogeneous or heterogeneous.

Homogeneous electrocatalysts refers to transition metal complexes, which performs the electroreduction of CO_2 at cathode to provide the reduction products. These metal complexes are dispersed in bulk electrolyte. The main reason why homogeneous catalysts are used is the inertness of carbon dioxide molecule which acts as a major setback for the reduction of carbon dioxide. Thus it is co-ordinated with transition metals to lower the activation energy required.

In **heterogeneous electrocatalysts** a thin film or coating of catalysts particles is deposited on electrode surface and as a result of which variety of reaction products like alcohols, hydrocarbons, formic acids are formed. However the reaction mechanism of both the catalysts is different and both require different electrochemical cell designs and the experimental protocol is also different. While performing this electrochemical reduction one thing that we should keep in mind is that it occurs at great negative over potentials and is also restricted by hydrogen release as a competitive reaction in

aqueous electrolyte. Thus the catalyst should be designed in such a way that should be capable enough to surmount these limitations.

1.8 Nature of Product

The product that is formed from electro reduction of carbon dioxide depends on pH, type of electrolyte and on the type of electrode material[2]. In this thesis report we will mainly focus on the electrochemical reduction of carbon dioxide via heterogeneous catalyst *i.e*. Cu_2O. We assess the role of graphene as a supporting catalyst for carbon dioxide reduction in aqueous solution as it provides large surface area for the active sites of Cu_2O and also increases the electron mobility that promote CO_2 reduction activity.

1.9 Objective of thesis

The overall objective of this project is to develop a monometallic electrocatalyst for conversion of CO_2. The detailed objectives are

- Synthesis of support (graphene oxide).
- Characterisation of the support for appropriate properties.
- Synthesis and doping of monometallic metal oxide (Cu_2O) on the graphene support.
- Characterisation of synthesised monometallic metal oxides electrocatalyts for conversion of carbon dioxide to fuel.

1.10 Overview of thesis

This thesis has been divided into **five chapters.**

Chapter one (Introduction) presents the current environmental problems and the brief description of carbon dioxide utilisation. It covers the various greenhouse gases especially carbon dioxide and its harmful effects. Various approaches to combat the problem of carbon dioxide have also been discussed in this chapter and provide the objectives of this research.

Chapter two (Literature review) discusses and compares the studies conducted by various research groups using different metal, metal oxide and metal complex eletrocatalysts for electrochemical reduction of carbon dioxide to various products.

Chapter three (Experimental methods) shows the blueprint of experimental work performed in this research. This chapter is further divided into three parts namely

materials, experimental methods for synthesis and information about characterisation techniques used for the characterisation of the synthesised products.

Chapter four deals with the results and discussions. It discusses the data obtained by various characterisation techniques and further analyses has been done.

Chapter five (conclusions and recommendations) summarizes the data reported and also gives some recommendation for future research.

At the end, the references cited in the thesis have been listed.

Chapter 2

LITERATURE REVIEW

Overview

This Chapter describes the research papers that were studied for the purpose of literature survey. It explains the detailed summary of the research work of other research groups.

R.A Geioushy *et.al* performed the electroreduction of CO_2 to C_2H_5OH using high efficiency graphene/Cu_2O electrode. The reduction showed a noteworthy enhancement in current density due to graphene contribution. Very low loading of graphene/Cu_2O was done which resulted in great conversion of carbon dioxide to ethanol. The LSV showed a high current density value of 12.2mA/cm^2at -1.7V vs Ag/AgCl when compared to Cu_2O electrode (8.4mA/cm^2). The principal liquid product was ethanol with F.E of 9.93% at-0.9V vs Ag/AgCl. No other products or liquid products were detected which shows the selectivity of the reaction[2]. Michael Schwartz *et. al* reduced the carbon dioxide to alcohols using perovskite type catalysts. They recognized the ability of perovskite type oxides $La_{1.8}$ $Sr_{0.2}$ CuO_4 to perform the reduction of carbon dioxide electrochemically to alcohols when incorporated in the electrocatalyst region of the gas diffusion electrodes. Consistent results were obtained with carbon dioxide hydrogenation at Copper and $LaMn_{1-x}$ Cu_X O_3-α catalyst at higher temperature where Copper only gave hydrocarbons and catalysts having copper that is oxidised performs alcohols formation[3]. Kohjiro Hara *et.al* used gas diffusion electrode containing Pt catalyst under high pressure to perform the high efficiency electroreduction of carbon dioxide. The high efficiency electroreduction of carbon dioxide was done on Pt-GDE having the partial current density of 415 mA cm^2 [4].Li liu *et.al* modified the transistion metals and studied their influence on oxide derived copper for electroreduction of carbon dioxide. The effect of modified Ni, Zn and Au of oxide derived copper electrode on reduction of carbon dioxide was studied and it was found that the formic acid was the major product that was formed. The electrode that was modified with nickel showed the maximum faradic efficiency towards the formation of propanol and formic acid. The alcohol products were detected at applied reduction potentials ranging -1.4 to-1.6V .The faradic efficiency of formic acid was 30% and of propanol and ethanol was 2.7% and 1.6% respectively at -1.5V[5].

Dinghui Chi *et.al* morphologically controlled the CuO nanoparticles for electroreduction of carbon dioxide to ethanol. They synthesised CuO nanoparticles with high specific surface area and five morphologies by simple methods. They were further electroreduced by insitu methods to copper for reduction of CO_2. The electrocatalytic activity was studied by various methods[6]. Surya singh *et.al* used the salen ligands and the complexes of salen ligands as electrocatalysts for reduction of gaseous CO_2 to value added products electrochemically. They synthesised the salen ligands and their corresponding nickel and copper complexes and their applications as electrochemical catalysts was studied. They were found to be capable of electrochemical reduction and resulted in the formation of hydrocarbons and CO. The F.E was about 74% for Ni complex and 25% for Cu complex at 1.5V and 1.8V respectively. Nickel showed better performance because of its low stability, moreover copper was more selective towards hydrocarbons as compared to the nickel. They also reduced the overpotential of the metal complexes between 10-25% as compared to the pure metal counterparts to form various kinds of products[7]. Jingjie wu *et.al* produced a metal free electrocatalyst for the reduction of carbon dioxide to multi carbon hydrocarbons and oxygenates. They synthesised NGQDs which acted as a catalyst for the electrochemical reduction process. The carbon dioxide reduction with high F.E upto 90% was achieved with selectivity for ethylene and ethanol conversion upto 45%.[8]Jing Yuan *et.al* reduced carbon dioxide to ethanol over an active catalyst and that was copper supported on titania. They used citrate protecting method to obtain different Cu/TiO_2 catalysts. After the synthesis of these catalysts they performed and studied the electrochemical reduction of CO_2 to ethanol on Cu/TiO_2 electrodes in a CO_2 saturated KI aqueous solution. Among all the catalysts synthesised the one with the 40 wt% showed the highest electrolytic activity with the total F.E (around 33.6%) around 8 times higher than the other catalysts. Moreover they also proved that the catalyst with 40wt% shows amazing stability during 25 hr electrochemical process[9].

Dan Ren *et.al* selectively reduced CO_2 to ethanol and ethylene on Cu_2O catalysts. They first synthesised the Cu_2O layers by using that flat Cu discs as a substrate. They then further examined the electro reduction of CO_2 to C_2H_5OH and C_2H_4 at different potentials. They varied the thickness of Cu_2O overlayers and tuned the faradic yields steadily. The 1.7-3.6µm thick films showed the most efficient C-C bond formation to produce ethanol and ethylene with F.E 9-16% and 34-39% respectively[10]. Behnamfar *et.al* prepared Gd_2O_3 nanoparticles by calcinations of new Gd complex precipitates in air at different temperature, and further

studied their catalytic activity for electrochemical reduction of CO_2 in water,the nanoparticles were characterised by FESEM and XRD analyses. They used 3 electrode system for their electrochemical studies in which they used Glassy carbon as a working electrode and silver wire as a pseudo reference and Pt electrode as a counter electrode. The main reduction product was CO[11]. Ullah *et.al* reduced CO_2 electrochemically in an aqueous electrolyte using an Iridium/Ruthenium oxide electrode .The aqueous electrolyte used was Briton Robinson buffer, whose pH is 5.82.The reduction experiment, was performed at -1.7V and the rate was dependent on electrode potential. Ethanol was the major product formed with small quantities of methanol, acetone and acetaldehyde[12]. Lan *et.al* loaded Cu (core)/CuO (Shell) catalyst in a three electrode cell which further gives information about the transformation between Cu, Cu^1 and CuO species. They further performed electro reduction experiments in a flow reactor at 25ºC under atmospheric pressure. They also used Nafion to separate anode and cathode. The experiments resulted in the reduction of carbon dioxide to CO and HCOOH they further found that the faradic efficiencies of the products were higher at loading of 1.0 mg/cm^2 [13]. Sharma *et. al* reported their studies of using TiO_2-x and TiO as a electrocatalysts to convert carbon dioxide to fuels by incorporating the electrocatalysts in an electrochemical cell. They synthesised non-stoichiometric TiOx (γ-Ti_3O_5) under appropriate required conditions and found that the product formed from reduction of carbon dioxide was CO [14].

Andrews *et.al* performed the electro reduction of carbon dioxide in aqueous bicarbonate electrolytes and by using Cu nanoclusters supported on ZnO electrodes. They fabricated the electrodes using single crystal ZnO substrates after that vacuum deposition of Cu was done. They further characterised them by STM. The reduction gave the gaseous end products like H_2, CO, CH_4 and the liquid end products were methanol, formate and ethanol with small amount of propanol [15]. Li *et.al* annealed the Cu foil in air and after that they electrochemically reduced the Cu_2O layers and formed the modified electrodes. The Cu_2O layers were formed at 500ºC and were ≥3μm thick. The electrochemical experiment was performed in 2 compartment cell and the products formed for CO_2 reduction were CO,HCOOH, C_2H_4[16]. Keerthiga *et.al* performed the electrochemical reduction of CO_2 with surface oxidised Cu with the help of unmodified Cu electrode. The electrolyte used was KCl and the reduction product was a hydrocarbon (C_2H_6) with the total FE of 27%[17]. Le *et.al* reduced CO_2 to CH_3OH directly using Cu_2O electrodes. The F.E of the product formed was around 38%. The results indicate that CH_3OH yields are dynamic and Cu_2O are reduced to metallic Cu[18]. Ohya *et.al* reduced the CO_2 to hydrocarbons using Cu_2O supported on Zn disk.

The reduction products were CH_4 and C_2H_4 with the FE of 7.5 and 6.8% respectively[19]. Yano *et.al* performed pulse mode electrochemical reduction for reduction of CO2 to ethylene using Cu and Cu_2O electrodes. The F.E of the product formed was 28%[20]. Qu *et.al* synthesised RuO_2/TiO_2 composites and used them with Pt support for conversion of CO_2 to $CH_3OH$with FE of 60%[21]. R.A Geioushy *et.al* performed the reduction of CO_2 to C_3H_7OH electrochemically using Cu2O/ ZnO graphene electrode. Very small loading of Cu_2O/ ZnO was done which resulted in conversion of carbon dioxide to propanol[22].

Ma *et.al* studied and presented the effect of Cu nanowire on selective electrocatalytic reduction of CO_2.They also showed that with the increase in Cu nanowires length the formation of propanol was detected along with CO, HCOOH and C_2H_4 (major product),moreover further increase in length of Cu nanowires the formation of ethanol and ethane occurred[23]. Apart from these many research groups reduced carbon dioxide to various value added products using metal oxide, metals and metal complexes respectively as an electrocatalysts and that information is summed up in a tabular form given below.

Table 2.1 Studies on electroreduction of carbon dioxide using metal oxide electrocatalysts during 1989-2015

S. No.	Metal oxide	Support/ Promoter	Working Electrode	Other electrodes		Electrolyte		Reaction condition(s)			Observations		References
				Anode	Reference electrode	Concentration	pH	Temp. /Pressure	V	CO_2 flow rate	Product (FE %)	Current density (mA/cm^2)	
1	Cu_2O films	_	_	_	_	0.1M $KHCO_3$	_	25°C	-0.99	_	C_2H_4(34-39) C_2H_5OH (9-16) CH_4	_	[10]
2	Gd_2O_3 nanop-articles	_	GCE	Pt	Ag wire	0.1M TBAH/CH_3CN	_	25°C, 1atm	-1.88	_	CO	_	[11]
3	CuO nanopar-ticles	_	_	_	_	O.2M KI	_		1.5	_	C_2H_5OH (35) C_3H_7OH (5)	_	[6]
4	$Ir_{0.8}$ $Ru_{0.2}$-oxide	Flat Ti Surface	_	Graphite rods	Mercury/ mercurous	0.4M Briton Robinson buffer solution	5.8	4°and 22°C, 1atm	-1.7	_	C_2H_5OH (96 at 4°and 85 at 22°C)	_	[12]
5	CuO (shell)	Cu (core)	_	_	_	1M $KHCO_3$	_	25°C, 1atm	_	_	CO(23) HCOOH (20) CH_3OH (1-3)	_	[13]
6	γ-Ti_3O_5	_	_	_	_	_	_	_	1-2.5	_	CO (7), HCOOH (10)	_	[14]
7	ZnO	_	_	_	_	0.1M $KHCO_3$	_	_	-	_	CO (5.4),	_	[15]

	decorated with Cu nanoclusters								1.20		CH_4 (1.8), C_2H_4 (10), CH_3OH, 2.8), C_2H_5OH (10), HCOO- (8)		
8	Cu from thick Cu_2O films	_	_	_	_	0.5M $NaHCO_3$	_	_	Q≥~ 5 C·cm-2	_	CO (45), HCOOH (33) C_2H_4(5) C_2H_6 (10)	_	[16]
9	Surface oxidized Cu	_	Cu	_	_	0.5M KCl	_	25ºC	_	_	C_2H_6 (27)	_	[17]
10	Electrodeposited Cu_2O		_	_	_	$KHCO_3$	7.6	25ºC	_	_	CH_3OH (38)	_	[18]
11	Cu_2O	Zn disk	_	_	_	KOH/ methanol	7.5	-30ºC,	_	_	CH_4 (7.5) C_2H_4 (6.8)	_	[19]
12	Cu_2O	Cu plate	_	_	_	$KHCO_3$	_	25°C, 1 atm	_	_	C_2H_4 (22) C_2H_4 (28)	_	[20]
13	RuO_2/ TiO_2	Pt	_	_	_	0.5M $NaHCO_3$	_	25°C, 1 atm	_	_	CH_3OH (60.5)	_	[21]

	composites												
14	Cu_2O	Graphene	_	_	_	0.5M $NaHCO_3$	_	_	-0.9	_	C_2H_5OH (9.93)	12.2	[2]
15	Cu_2O/ ZnO	Graphene	_	_	_	0.5M $NaHCO_3$	_	_	-0.9	_	C_3H_7OH (30)	12.2	[22]
16	$Cu(OH)_2$	Cu nanowires	_	_	_	0.1M $KHCO_3$	_	_	-1.1	_	C_2H_4 17.4	_	[23]
17	SnO	ZnSe ATR-IR	Sn foil	Pt mesh	_	3M NaCl	_	_	-1.4- -1.8	_	H_2, $HCOO^-$,CO	_	[24]
18	TiO_2	Cu	_	_	_	0.2 M KI	_	_	- 1.45	_	C_2H_5OH (27.4%)	8.66	[9]
19	Cu_2O		_	_	_	0.1M $KHCO_3$	_	_	- 0.99	_	C_2H_4(39 %) C_2H_5OH (9-16%)	_	
20	Co_3O_4	Zn	_	_	_	0.5M $KHCO_3$	_	_	1.5		HCOOH (78.5%)		[25]
21	Cu_2O	Carbon paper				PAA/PVA/KOH SPE		25°C	3	20 ml/min	CH_3OH CH_4 CO	8.1	[26]
22	MoS_x	PEI modifiedgraphene	GCE	Pt wire	Ag/Agcl	0.5M $NaHCO_3$	_	_	- 0.65	_	CO (85.1%)	_	[27]
23	Cu_2O	Carbon paper		Pt/C		SPE	_	_	2.5	_	CH_3OH CH_4	_	[28]

24	Oxide derived Cu electrode	Ni, Zn, Au	Cu foil	Pt plate	_	0.1M $NaHCO_3$	_	_	-1.2 to-1.6	_	HCOOH C_3H_7OH C_2H_5OH	_	[5]
24	TiO_2	Graphene											
25	ZnO/ Al_2O_3	Cu	_	_	_	_	_	160^0C	_	30 ml/min	C_2H_5OH	_	[29]
26	Cu_2O	Cu disks	_	Pt wire	Ag/Agcl	0.1M $KHCO_3$	_	_	_	20 sccm	C_2H_4 (42.6%) C_2H_5OH (11.8%) C_3H_7OH (5.4%)	-13.3 -3.7 -1.7	[30]
27	Cu_2O	Graphite plates	_	Co_3O_4	_	0.5M $KHCO_3$	_	_	2	_	C_2H_5OH (96.1%) HCOOH	4.5	[31]
28	Cl induced bi phasic Cu_2O-Cu	_	Cu	Pt plate	Ag/Agcl	O.1M Kcl	_	_	-0.6 to -1.8	_	C_3H_7OH (8.7%) C_4H_{10} C_2H_4 C_2H_5OH	_	[32]

Table 2.2 Studies on electroreduction of carbon dioxide using metal electrocatalysts during 1989-2015

S. No.	Metal	Support/ Promoter	Working Electrode	Other electrodes		Electrolyte		Reaction condition(s)			Observations		References
				Anode	Reference electrode	Concentration	pH	Temp. /Pressure	V	CO_2 flowrate	Product (FE %)	Current density (mA/cm^2)	
1.	Cu	_	_	_	_	0.45M $KHCO_3$	_	25˚C	_	_	$HCOO^-$ (86)	22	[33]
2.	Ni	_	_	_	_	0.5 M $KHCO_3$	_	25˚C, 1atm	_	_	HCOOH (29), CO (1.7)	_	[34]
3.	Zn	_	_	_	_	MeOH+ NaOH+ Cu particles	_	-30˚C	_	_	HCOOH (7), CO (60), CH_4 (12)	_	[35]
4.	Cu mesh	_	_	_	_	0.45 M $KHCO_3$ + 1 M KCl	_	26˚C, 1.4 atm	_	_	$HCOO^-$ (86)	130	[36]
5.	Sn	_	_	_	_	0.5 M $KHCO_3$ + 2 M KCl	7.5	18˚C, 1 atm	_	_	$HCOO^-$ (91)	60	[37]
6.	Cu-Ni	_	_	_	_	$KHCO_3$ + MeOH (8:2)	_	-5˚C	_	_	HCOOH (13), CO (4), HCs (26)	_	[38]
7.	Pb	_	_	_	_	K_2HPO_4	7	25˚C, 1 atm	_	_	$HCOO^-$ (93)		[39]
8.	Pb	_	_	_	_	NaOH	8.5	21˚C	_	_	$HCOO^-$ (70)	2.5	[40]
9.	Cu	_	_	_	_	0.5 M K_2HPO_4	_	25˚C,	_	_	HCOOH	_	[41]

								1 atm			(6), CO (40), HCs (30)		
10.	Cu mesh	_	_	_	_	$KHCO_3$	_	25˚C, 1 atm	_	_	CH_4 (19.4), C_2H_4 (18.7)	_	[42]
11.	In	_	_	_	_	$NaHCO_3$	8		_	_	$HCOO^-$ (45)	40	[43]
12.	Fe	_	_	_	_	0.5 M H_2SO_4		25˚C, 1 atm	_	_	CH_4, HCHO, C_2H_6, C_2H_5OH	_	[44]
13.	Pb	_	_	_	_	0.45 M $KHCO_3$ + HCl		25˚C, 1 atm	_	_	$HCOO^-$ (57)	10.5	[45]
14.	Bi/GC	_	_	_	_	CH_3CN		25˚C, 1 atm		_	CO (95)	_	[46]
15.	Sn/GDE	_	_	_	_	$NaHCO_3$	8.3	25˚C	1.6	_	$HCOO^-$ (70)	_	[47]
16.	Sn	_	_	_	_	$KHCO_3$	6.98	25˚C, 1 atm		_	$HCOO^-$ (91)	_	[48]
17.	Ag	_	_	_	_	BMImCl + 20 wt% H_2O		25˚C, 1 atm		_	CO (>99)	_	[49]
18.	Cu nanoc-ubes	_	_	_	_	0.1 M $KHCO_3$	_	_	0.60	_	C_2H_4	_	[50]
19.	Cu meso-crystals	_	_	_	_	0.1 M $KHCO_3$	_	_	0.99	_	CH_4 (1.5), C_2H_4 (27.2)	_	[51]

20.	Cu	_	_	_	_	0.1 M $KHCO_3$	_	_	-1.3	_	EtOH (6.9),Pr^nOH (3.0)	5	[52]
21.	GDE	_	_	_	_	0.5 M KOH	_	_	-2.6	_	EtOH(5), Pr^nOH (1),C_2H_4 (69), CH_4(9)	180	[3]
22.	GDE/Pt	_	_	_	_	0.5 M $KHCO_3$	_	_	-1.7	_	EtOH (2.2), MeOH (35)	19.8	[4]
23.	Sn	_	_	_	_	0.5 M $KHCO_3$	_	_	2	_	HCOOH (92.6)	_	[53]
24.	Sn	Graphite plate		Co_3O_4		0.5 M $KHCO_3$			2	_	HCOOH (57.9)	_	[54]
25.	In	_	_	Pt foil	_	dimcarb	_	25˚C	-1.34	_	$HCOO^-$ (40), CO (45)	_	[55]
26.	Zn	Graphite plate	_	Co_3O_4	_	0.5 M $KHCO_3$	_		2.3	_	HCOOH (45.33)	_	[56]
27.	Cu	Graphite	_	IrO_2	_		_	90˚C	-1.54	_	MeOH (75)	-30	[57]

28.	Ag	Cu foil	_	Pt gauze	Ag/AgCl	0.5 M $KHCO_3$	_	RT	-1.7	_	CO (64.6)	_	[58]
29.	Bi	Cu foil	_	Pt	Ag/AgCl	0.1 M $KHCO_3$	_	_	-1.5	_	$HCOO^-$ (91.3)	_	[59]
30.	Sn	Oxide layer	_	_	Ag/AgCl	0.1 M $KHCO_3$	_	_	-1.8	_	$HCOO^-$ (84)	_	[60]
31.	Sn		_	_	Ag/AgCl	0.1 M $KHCO_3$	6.8	_	-0.9	_	HCOOH (70)	_	[61]
32.	Cu	Porous carbon	_	Pt/C		Amberlyst/SPEEK	_	_		_	HCOOH (0.7), CO (16)	3.3	[62]
33.	Sn/S_2	Reduced graphene oxide	Glassy carbon (3 mm)	Pt wire	Ag/AgCl	0.5 M $NaHCO_3$	_	22˚C	0.68	_	$HCOO^-$ (84.5)	13.9	[63]

CHAPTER 3

EXPERIMENTAL SECTION

This chapter presents the experimental details of synthesis of graphene oxide and graphene embedded Cu_2O electrocatalysts along with the detail description through block diagrams. Moreover this chapter also discusses about the characterisation techniques and the instruments that are used for characterisation of formed products.

3.1. Materials

Pure graphite powder, sodium hydroxide pellets, concentrated sulphuric acid, sodium nitrate, sodium lauryl sulphate (99%), potassium permanganate, hydroxylammonium chloride (99%), hydrogen peroxide (30% concentration, w/v), sodium hydroxide (98%), cupric chloride and zinc chloride were purchased from M/s. LOBA Chemie Pvt. Ltd. Ethanol (99.9%, v/v) was purchased from M/s. Changshu Hongsheng Fine Chemicals. All the reagents and chemicals used were of analytical grade and were used without any further purification.

3.2. Methods

3.2.1 Synthesis of graphene oxide (GO)

Graphene oxide was synthesized by using Hummer's method. In a 500 ml round bottom flask; 2 g pure graphite powder, 1 g $NaNO_3$ (sodium nitrate) and 46 ml H_2SO_4 sulfuric acid (conc.) were mixed. The flask was immersed in ice-water bath at 0˚C and rigorous stirring was done for 15 minutes. Then, slow addition of 6 g $KMnO_4$ (potassium permanganate) was done to the above solution and it was allowed to cool for 15 minutes. The suspension was stirred for 1 h continuously and then 92 ml of distilled water was added slowly for 10 minutes. Subsequently, the suspended solution was diluted by adding 280 ml of warm water. The solution was treated with 10 ml of H_2O_2 (30%w/v) to reduce residual permanganate to soluble manganese ions. The resulting suspension was filtered, washed with water and dried in vacuum oven for 24 h at 60 ˚C and black coloured powdered product was formed.

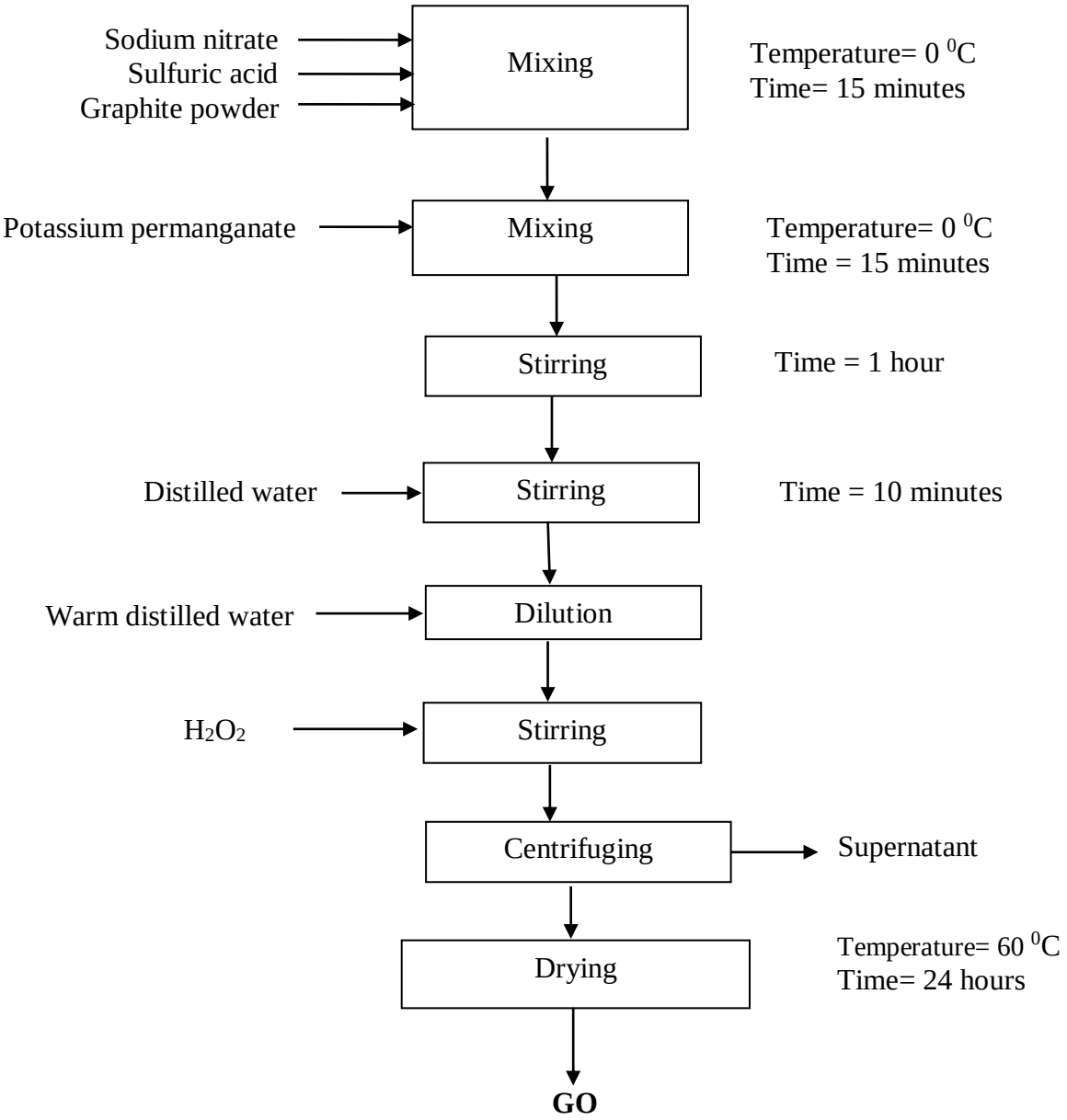

Figure 3.1: Block diagram for synthesis of graphene oxide (GO)

3.2.2 Synthesis of graphene-embedded Cu_2O electrocatalyst

GO stock solution (1 mg/ml) was prepared and sonication was done for 2 h. From the stock solution, 3 ml was pipetted out and dissolved in 15.1 ml of ultrapure water. Then sonication of solution was done for 30 minutes. After that, 0.45 ml of $CuCl_2$ (0.1 M) and 0.087 g SDS were mixed with the solution under rigorous stirring. 0.9 ml of NaOH (1.0 M) was added followed by rapid injection of 4 ml of $[NH_3OH]^+Cl^-$ (0.1 M) in above solution mixture, undergone stirring for 30 minutes. After that centrifugation of suspension was done and it

was washed with ethanol and water repeatedly. Yellow brown precipitates were formed and this was dried in vacuum oven for 18 h at 40˚C.

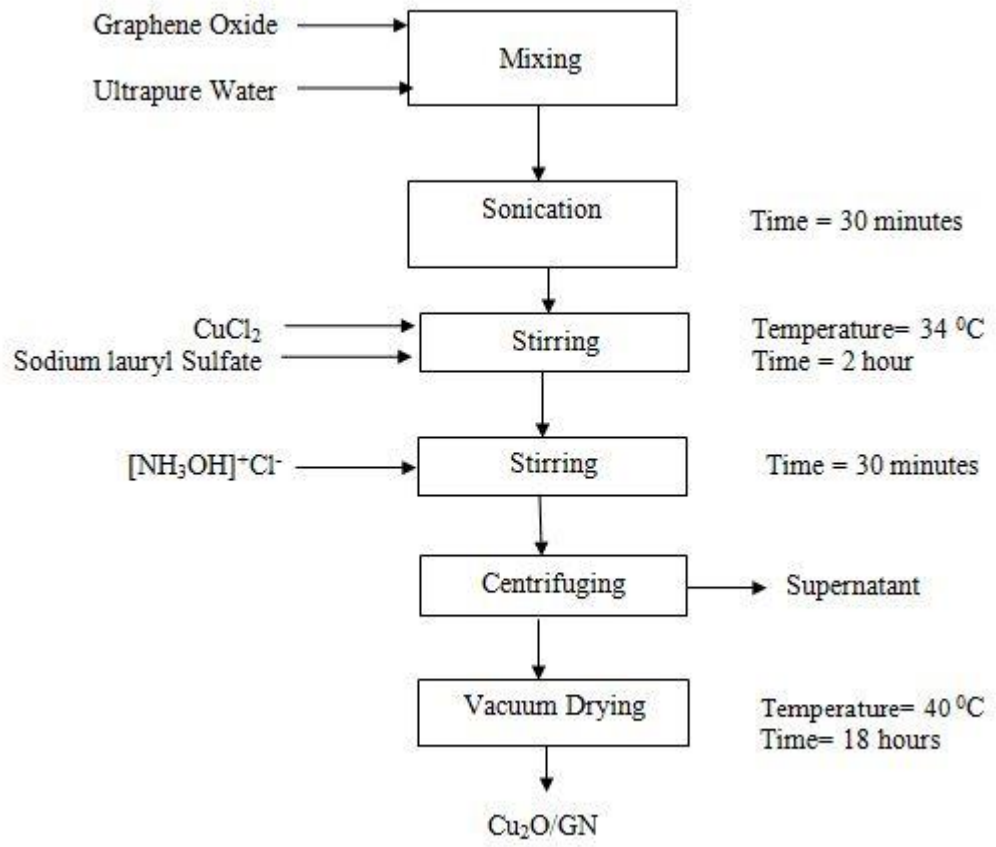

Figure 3.2: Block diagram for synthesis of Cu_2O/GN electrocatalyst

3.3 Characterisation Techniques:

Characterisation is defined as the procedure by which the properties and structure of the material are studied. Here in this experiment we have used a variety of characterisation methods for identification of the catalysts formed.

The techniques used here are:

- XPS
- Raman Spectra
- FESEM

3.3.1 XPS: X-ray photoelectron spectroscopy is also known by name ESCA (i.e. Electron spectroscopy for chemical analysis), it a classical technique that is used to analyse the surface composition that include the elemental composition of surface, empirical formula and

electronic state of each element.XPS measurements were carried out to identify oxygen, zinc and copper moieties on synthesized nanoparticles. It was carried on Kratos axis ultra DLD system using a monochromatic Al-Kα source operated at anode potential of 15 kV. The survey spectra were recorded with a pass energy of 50 eV while the high resolution spectra with a pass energy of 20 eV and emission current of 10 mA. Pressure in analysis chamber was maintained at 2×10^{-9} torr. Data processing was performed using the XPS peak 4.1 software and the core level spectra were fitted with mixed Gaussian-Lorentzian convoluted function (80/20) and Shirley function was used for background substraction.

3.3.2 Raman spectra: Raman spectroscopy is a spectroscopic technique for carbonaceous characterisation which gives information about rotational and vibrational modes. A Raman spectrum is a distinct chemical fingerprint for a particular molecule and is used to identify the chemical structure and identity of a molecule. Here we have studied the Raman spectra of GO and GN/Cu_2O composites. Raman spectra of the samples were obtained using a confocal Raman microscope (WITec alpha 300R, Germany) with λ = 532 nm laser excitation to evaluate any structural changes occurring in the synthesized sample. It was also used to examine the presence and position of D-(disordered) and G-(graphitic) bands and their intensity ratio.

3.3.3 FESEM: This characterization technique is used to determine the surface morphologies of the synthesized sample. FE-SEM is more advanced form of SEM which provides energy beam of high quality and narrower nature. This provides better image quality and resolution. This technique is able to done sample magnification higher than the range of 10Kx. The surface morphology of sample was analyzed by field emission scanning electron microscope (JEOL JSM – 6510 LV) at an accelerating voltage of 20 kV. To avoid sample charging problems, the sample was coated with gold of thickness 50 μm with the help of automatic sputter coater (Polaron).

CHAPTER 4

RESULTS AND DISCUSSION

To determine wheter the prepared electrocatalyst is suitable for electrochemical reduction of CO2,it was further characterised by different techniques like XPS, Raman spectroscopy and FESEM. And the details and results of characterisation techniques are explained as follows:

X-ray photoelectron spectroscopy analysis: The composition and valence state of elements are confirmed by XPS analysis. Fig. 4.1a shows the fully scanned XPS spectrum in the range of 0-1100 eV. From these fully scanned spectra, only C, O and Cu elements were observed. Fig. 4.1b shows the high resolution spectra for C1s region at 285 eV, which can be deconvoluted into three peaks. C1s binding energy peaks at 284.8 eV 286.06 eV and 288.4 eV which were attributed to C-C, C-O and C=O bands, respectively.[64] O 1s region at 530 eV high resolution spectra shown in fig. 4.2c, after deconvolation into three different peaks at 530.61 eV, 531.7 eV and 532.7 eV which were attributed to OH, C-O, and C=O bands, respectively. Moreover, a peak characteristic of Cu 2p3/2 of the Cu (I) oxidation state at 932.2 eV also appeared as shown in Fig. 4.2d. The Cu 2p1/2 peak at 952 eV corresponds to Cu (II) oxidation state. [2,22,64]

Table 4.1 shows variation in C 1s, O 1s, and Cu 2p in binding energy, FWHM and area%.

Sample	Parameter	C1	C2	C3
Cu_2O/GN	**BE (eV)**	284.8	286.06	288.4
	FWHM	1.02	1.62	2.73
	A%	55.29	28.56	16.13
		O1	**O2**	**O3**
	BE (eV)	530.61	531.7	532.7
	FWHM	0.99	1.46	1.47
	A%	**31.55**	**68.05**	**0.3879**
		Cu 2P3/2	**Cu 2P1/2**	

	BE (eV)	933.15	953.05	
	FWHM	1.48	2.38	
	A%	61.94	38.05	

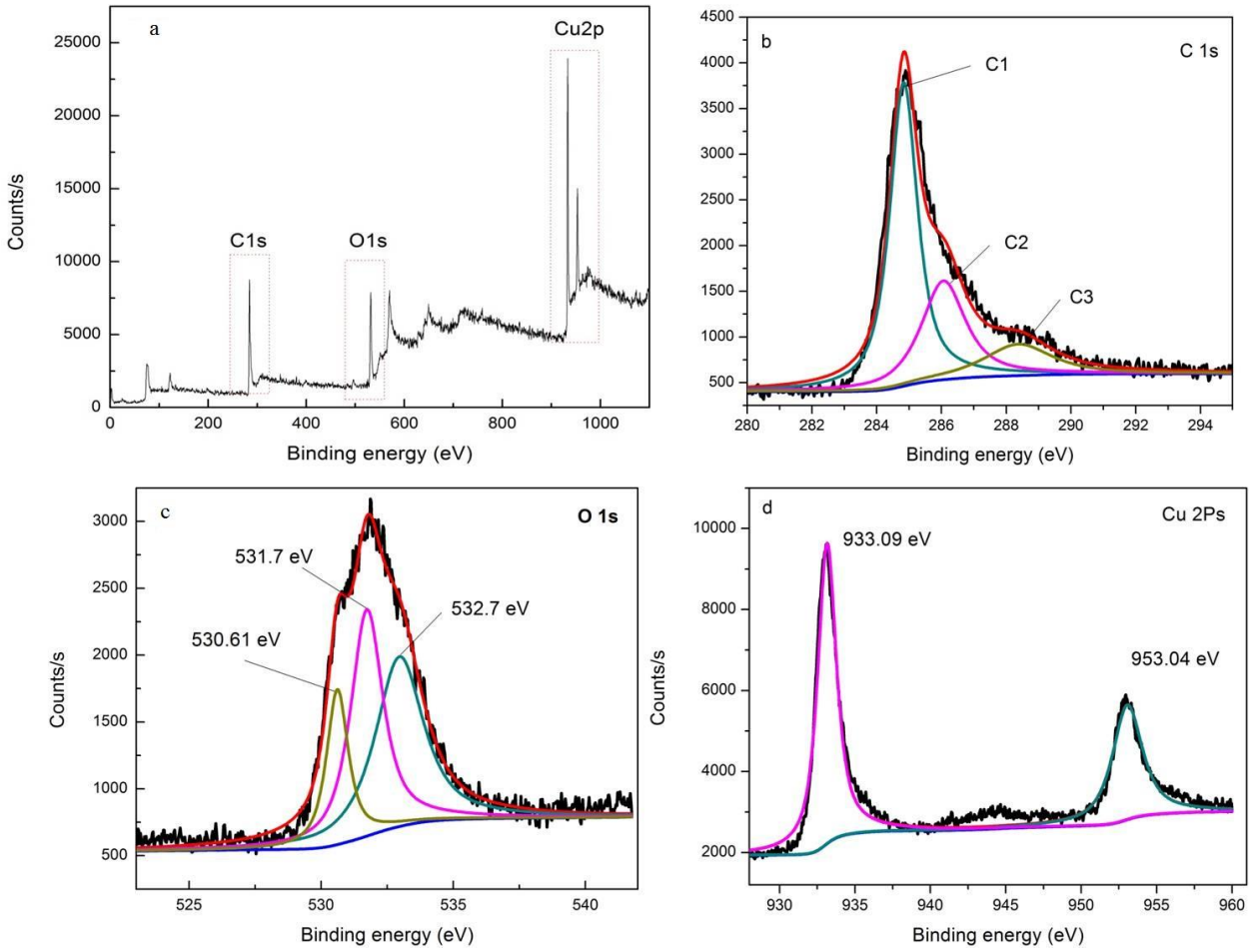

Figure4.1 (a) Full scan XPS spectra for Cu_2O/GN, deconvolation of (**b)** C 1s scan, (**c)** O 1s scan, (**d)** Cu 2P scan

Raman Spectroscopy: Order and disorder in carbon crystal structure is distinguished by Raman spectroscopy and it is powerful nondestructive technique. The typical raman spectra for graphene oxide and Cu_2O/GN is shown in fig. 4.2. Both the spectra shows D band and G band existence at 1350 and 1586 cm^{-1}. The intensity ration of D to G band (i.e.I_D/I_G) was observed for graphene oxide is 0.9733 and for Cu_2O/GN is 1.022. This increase in I_D/I_G from graphene oxide to Cu_2O/GN is because of chemical reduction of graphene oxide.[2] After chemical reduction, the graphene network will be re-established, however it appears smaller in size than original graphene oxide[65].

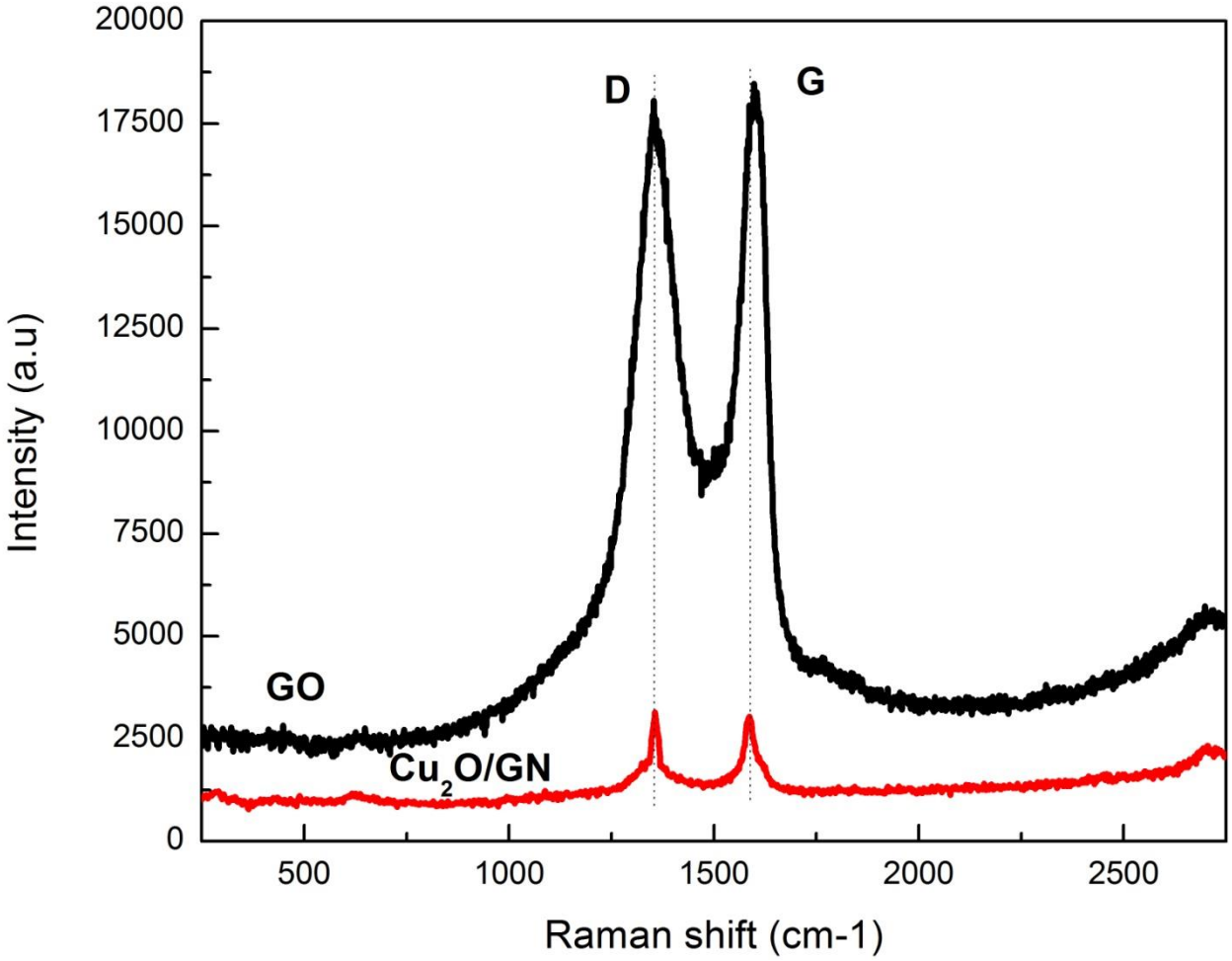

Figure 4.2 Raman spectra for graphene oxide (GO) and Cu_2O/GN

Field Emission Scanning Electron microscope (FESEM) analysis: The morphologies of as synthesized graphene oxide (GO) and Cu_2O/GN nanoparticles are shown in fig.4.3. Here the surface morphologies of GO and Cu_2O/GN are different. Graphene oxide shows the wrinkled layer morphology.[65] Also, it can be seen that Cu_2O deposited as small particles on its surface. Cu_2O shows the cubic morphology with the average edge length 200-300 nm.

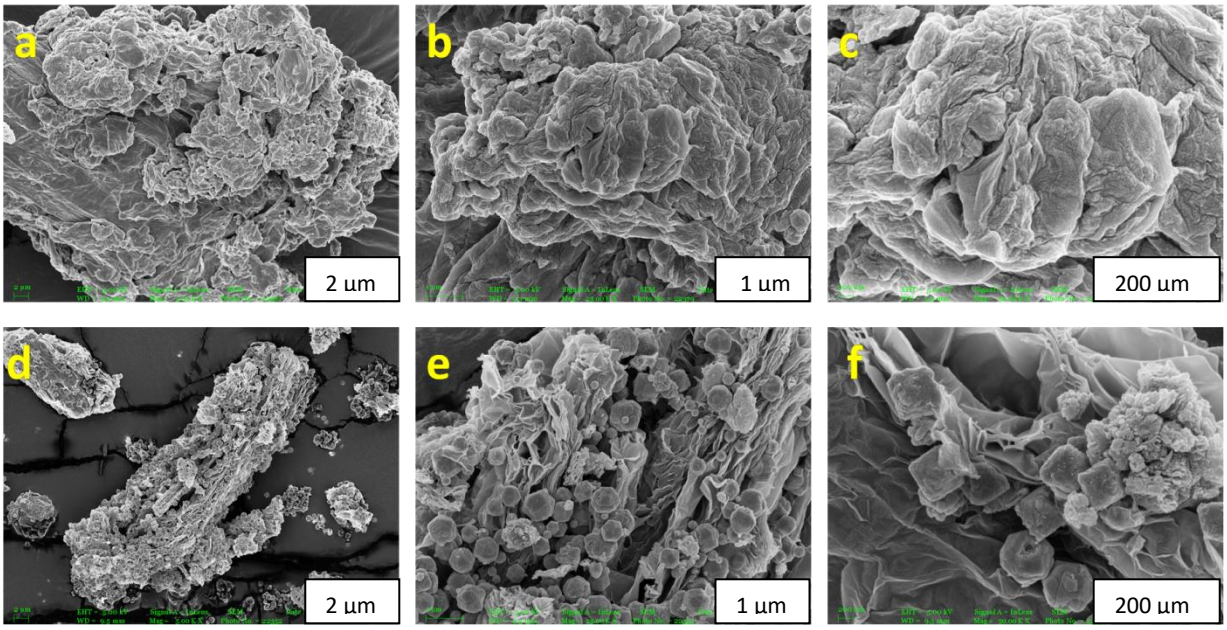

Figure.4.3 FE-SEM images of Graphene oxide (a,b,c) and Cu_2O/GN (d,e,f)

CHAPTER-5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

We have synthesised monometallic metal oxide (Cu_2O) on graphene supported electrocatalyst to be used for CO2 reduction. For that graphene oxide was first synthesised by Hummer's method and later it was doped with monometallic metal oxide. The prepared electrocatalysts were characterised by XPS, Raman spectra and FE-SEM to evaluate its potential as an electrocatalyst.

The XPS data obtained reveal information about the composition and valence state of elements. The XPS analysis report confirms the presence of C, O and Cu elements in prepared catalyst. A peak characteristic of Cu 2p3/2 of the Cu (I) oxidation state at 932.2 eV also appeared. The Cu 2p1/2 peak at 952 eV corresponds to Cu (II) oxidation state. The Raman spectra tell us about order and disorder of carbon crystal structure. The intensity ratio of D to G band (i.e.I_D/I_G) observed for graphene oxide was 0.9733 and for Cu_2O/GN was 1.022. Moreover the morphologies were studied with the help of FE-SEM, and it can be seen that Graphene oxide shows the wrinkled layer morphology and Cu_2O deposited as small particles on its surface. Cu_2O shows the cubic morphology with the average edge length 200-300 nm. The characterisation results of electrocatalysts are found suitable when compared with literature thus it implicate that these electrocatalysts can be used for electroreduction of carbon dioxide to fuel.

Recommendations for future work

Although prepared electrocatalyst is found its suitability as an electrocatalyst for CO_2 reduction the following further studies are recommended for the application of prepared electrocatalyst.

- There is a need to study the performance of prepared electrocatalyst in terms of selective production of desired products.
- Durability of the electrocatalysts is one of the major constrains in CO_2 electroreduction process. Hence, it is recommended to estimate the durability of prepared catalyst by experimentations.

- The prepared material can be further loaded with different metals and metal oxides and the formation of gaseous products can be examined.
- Moreover they can be further tuned with metals and metal oxides to study and increase their selectivity towards different gaseous products.

REFERENCES

(1) Abbas, A.; Ullah, M.; Ali, Q.; Zahid, I.; Abbas, S.; Wang, X.; TAYLOR & FRANCIS LTD 2-4 PARK SQUARE, MILTON PARK, ABINGDON OR14 4RN, OXON, ENGLAND: 2017.

(2) Geioushy, R.; Khaled, M. M.; Hakeem, A. S.; Alhooshani, K.; Basheer, C. *Journal of Electroanalytical Chemistry* **2017**, *785*, 138.

(3) Schwartz, M.; Cook, R. L.; Kehoe, V. M.; MacDuff, R. C.; Patel, J.; Sammells, A. F. *Journal of the Electrochemical Society* **1993**, *140*, 614.

(4) Hara, K.; Kudo, A.; Sakata, T.; Watanabe, M. *Journal of the Electrochemical Society* **1995**, *142*, L57.

(5) Liu, L.; Tian, N.; Huang, L.; Hong, Y.-H.; Xie, A.-Y.; Zhang, F.-Y.; Xiao, C.; Zhou, Z.-Y.; Sun, S.-G. *Chinese Journal of Catalysis* **2016**, *37*, 1070.

(6) Chi, D.; Yang, H.; Du, Y.; Lv, T.; Sui, G.; Wang, H.; Lu, J. *RSC Advances* **2014**, *4*, 37329.

(7) Singh, S.; Phukan, B.; Mukherjee, C.; Verma, A. *Rsc Advances* **2015**, *5*, 3581.

(8) Wu, J.; Ma, S.; Sun, J.; Gold, J. I.; Tiwary, C.; Kim, B.; Zhu, L.; Chopra, N.; Odeh, I. N.; Vajtai, R. *Nature communications* **2016**, *7*, 13869.

(9) Yuan, J.; Liu, L.; Guo, R.-R.; Zeng, S.; Wang, H.; Lu, J.-X. *Catalysts* **2017**, *7*, 220.

(10) Ren, D.; Deng, Y.; Handoko, A. D.; Chen, C. S.; Malkhandi, S.; Yeo, B. S. *ACS Catalysis* **2015**, *5*, 2814.

(11) Behnamfar, M. T. *Journal of Particle Science & Technology* **2015**, *1*, 21.

(12) Ullah, N.; Ali, I.; Jansen, M.; Omanovic, S. *The Canadian Journal of Chemical Engineering* **2015**, *93*, 55.

(13) Lan, Y.; Gai, C.; Kenis, P. J.; Lu, J. *ChemElectroChem* **2014**, *1*, 1577.

(14) Sharma, P. P.; Ke, F.-S.; Zhou, X.-D. *ECS Transactions* **2014**, *61*, 331.

(15) Andrews, E.; Ren, M.; Wang, F.; Zhang, Z.; Sprunger, P.; Kurtz, R.; Flake, J. *Journal of The Electrochemical Society* **2013**, *160*, H841.

(16) Li, C. W.; Kanan, M. W. *Journal of the American Chemical Society* **2012**, *134*, 7231.

(17) Keerthiga, G.; Viswanathan, B.; Pulikottil, C. A.; Chetty, R. *Bonfring International Journal of Industrial Engineering and Management Science* **2012**, *2*, 41.

(18) Le, M.; Ren, M.; Zhang, Z.; Sprunger, P. T.; Kurtz, R. L.; Flake, J. C. *Journal of the Electrochemical Society* **2011**, *158*, E45.

(19) Ohya, S.; Kaneco, S.; Katsumata, H.; Suzuki, T.; Ohta, K. *Catalysis Today* **2009**, *148*, 329.

(20) Yano, J.; Yamasaki, S. *Journal of applied electrochemistry* **2008**, *38*, 1721.

(21) Qu, J.; Zhang, X.; Wang, Y.; Xie, C. *Electrochimica Acta* **2005**, *50*, 3576.

(22) Geioushy, R.; Khaled, M. M.; Alhooshani, K.; Hakeem, A. S.; Rinaldi, A. *Electrochimica Acta* **2017**, *245*, 456.

(23) Ma, M.; Djanashvili, K.; Smith, W. A. *Angewandte Chemie International Edition* **2016**, *55*, 6680.

(24) Baruch, M. F.; Pander III, J. E.; White, J. L.; Bocarsly, A. B. *ACS Catalysis* **2015**, *5*, 3148.

(25) Yadav, V. S. K.; Purkait, M. K. *New Journal of Chemistry* **2015**, *39*, 7348.

(26) Aeshala, L. M.; Verma, A. In *Macromolecular Symposia*; Wiley Online Library: 2015; Vol. 357, p 79.

(27) Li, F.; Zhao, S.-F.; Chen, L.; Khan, A.; MacFarlane, D. R.; Zhang, J. *Energy & Environmental Science* **2016**, *9*, 216.

(28) Aeshala, L.; Uppaluri, R.; Verma, A. *Journal of CO2 utilization* **2013**, *3*, 49.

(29) Zhao, B.; Liu, Y.; Zhu, Z.; Guo, H.; Ma, X. *Journal of CO2 Utilization* **2018**, *24*, 34.

(30) Handoko, A. D.; Ong, C. W.; Huang, Y.; Lee, Z. G.; Lin, L.; Panetti, G. B.; Yeo, B. S. *The Journal of Physical Chemistry C* **2016**, *120*, 20058.
(31) Yadav, V.; Purkait, M. *Energy & Fuels* **2015**, *29*, 6670.
(32) Lee, S.; Kim, D.; Lee, J. *Angewandte Chemie* **2015**, *127*, 14914.
(33) Hori, Y.; Konishi, H.; Futamura, T.; Murata, A.; Koga, O.; Sakurai, H.; Oguma, K. *Electrochimica acta* **2005**, *50*, 5354.
(34) SHUANG, S.; ZHIQIAO, H.; JIEXU, Y.; JIANMENG, C. *High technology letters* **2006**, *12*, 333.
(35) Kaneco, S.; Ueno, Y.; Katsumata, H.; Suzuki, T.; Ohta, K. *Chemical Engineering Journal* **2006**, *119*, 107.
(36) Li, H.; Oloman, C. *Journal of Applied Electrochemistry* **2006**, *36*, 1105.
(37) Li, H.; Oloman, C. *Journal of Applied Electrochemistry* **2007**, *37*, 1107.
(38) Satoshi, K.; Yuki, S.; Hideyuki, K.; Tohru, S.; Kiyohisa, O. *Bulletin of the Catalysis Society of India* **2007**, *6*, 74.
(39) Subramanian, K.; Asokan, K.; Jeevarathinam, D.; Chandrasekaran, M. *Journal of Applied Electrochemistry* **2007**, *37*, 255.
(40) Innocent, B.; Liaigre, D.; Pasquier, D.; Ropital, F.; Léger, J.-M.; Kokoh, K. *Journal of Applied Electrochemistry* **2009**, *39*, 227.
(41) Ikeda, S.; Ito, K.; Noda, H. In *AIP Conference Proceedings*; AIP: 2009; Vol. 1136, p 108.
(42) Goncalves, M.; Gomes, A.; Condeco, J.; Fernandes, R.; Pardal, T.; Sequeira, C.; Branco, J. *Energy Conversion and Management* **2010**, *51*, 30.
(43) Narayanan, S.; Haines, B.; Soler, J.; Valdez, T. *Journal of The Electrochemical Society* **2011**, *158*, A167.
(44) Pérez-Rodríguez, S.; García, G.; Calvillo, L.; Celorrio, V.; Pastor, E.; Lázaro, M. *International Journal of Electrochemistry* **2011**, *2011*.
(45) Alvarez-Guerra, M.; Quintanilla, S.; Irabien, A. *Chemical engineering journal* **2012**, *207*, 278.
(46) DiMeglio, J. L.; Rosenthal, J. *Journal of the American Chemical Society* **2013**, *135*, 8798.
(47) Prakash, G. S.; Viva, F. A.; Olah, G. A. *Journal of Power Sources* **2013**, *223*, 68.
(48) Lv, W.; Zhang, R.; Gao, P.; Lei, L. *Journal of Power Sources* **2014**, *253*, 276.
(49) Zhou, F.; Liu, S.; Yang, B.; Wang, P.; Alshammari, A. S.; Deng, Y. *Electrochemistry Communications* **2014**, *46*, 103.
(50) Roberts, F. S.; Kuhl, K. P.; Nilsson, A. *Angewandte Chemie* **2015**, *127*, 5268.
(51) Chen, C. S.; Handoko, A. D.; Wan, J. H.; Ma, L.; Ren, D.; Yeo, B. S. *Catalysis Science & Technology* **2015**, *5*, 161.
(52) Hori, Y.; Murata, A.; Takahashi, R. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1989**, *85*, 2309.
(53) Yadav, V.; Purkait, M. *RSC Advances* **2015**, *5*, 68551.
(54) Yadav, V.; Purkait, M. *RSC Advances* **2016**, *6*, 40916.
(55) Chen, L.; Guo, S. X.; Li, F.; Bentley, C.; Horne, M.; Bond, A. M.; Zhang, J. *ChemSusChem* **2016**, *9*, 1271.
(56) Yadav, V. S. K.; Purkait, M. K. *Energy & Fuels* **2016**, *30*, 3340.
(57) Gutiérrez-Guerra, N.; Moreno-López, L.; Serrano-Ruiz, J.; Valverde, J.; de Lucas-Consuegra, A. *Applied Catalysis B: Environmental* **2016**, *188*, 272.
(58) Choi, J.; Kim, M. J.; Ahn, S. H.; Choi, I.; Jang, J. H.; Ham, Y. S.; Kim, J. J.; Kim, S.-K. *Chemical Engineering Journal* **2016**, *299*, 37.
(59) Lv, W.; Zhou, J.; Bei, J.; Zhang, R.; Wang, L.; Xu, Q.; Wang, W. *Applied Surface Science* **2017**, *393*, 191.

(60) Zhang, R.; Lv, W.; Lei, L. *Applied Surface Science* **2015**, *356*, 24.
(61) Feaster, J. T.; Shi, C.; Cave, E. R.; Hatsukade, T.; Abram, D. N.; Kuhl, K. P.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F. *ACS Catalysis* **2017**, *7*, 4822.
(62) Aeshala, L.; Rahman, S.; Verma, A. *Separation and purification technology* **2012**, *94*, 131.
(63) Li, F.; Chen, L.; Xue, M.; Williams, T.; Zhang, Y.; MacFarlane, D. R.; Zhang, J. *Nano Energy* **2017**, *31*, 270.
(64) Luo, C.; Li, D.; Wu, W.; Yu, C.; Li, W.; Pan, C. *Applied Catalysis B: Environmental* **2015**, *166*, 217.
(65) Ji, Z.; Zhu, G.; Shen, X.; Zhou, H.; Wu, C.; Wang, M. *New Journal of Chemistry* **2012**, *36*, 1774.

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