Utilization of Porous Cu and Ni-based Nanomaterials for Carbon dioxide Conversion

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Abstract

The present paper illustrate the most advance trend of formation of low cost transition porous nanomaterials as semiconductor for the photocatalytic reduction of CO_2 to methanol under visible light. The most important factor is to modify the photocatalytic activity and to simplify separation process which initiate a magnetic compound over magnetic nanocomposites or nanosheets. In utilization of low cost nanomaterial this review has mainly focused on the improvement such as mesoporous Ni-based and porous Cu-based nanocomposites fabrication, characterization and. The effects towards carbon dioxide conversion, hydrogen generation, and supercapacitors based on the physico-chemical properties, structure, photocatalytic activity are also discussed in detail.
Key words- Porous, Photocatalytic, Methanol, CuO, Magnetic, and NiO

Introduction
Overview
Statement of research problem

India is the developing country and is the second most populated country. The concentration of greenhouse gases is increasing rapidly due to natural disasters like volcano eruption and human activities like burning of fossil fuels, which result for most of global warming over the past 40 years. [1-3] It has caused serious threats to biotic as well as the abiotic world. The reduction in the concentration of carbon dioxide is a major concern by utilization it into the formation of useful products and also get rid of all the problems.[2-4] For this purpose nanomaterial is needed for the conversion of carbon dioxide into value added chemicals. When its concentration become 1% or above it, it will make some people feel lethargic and gives a stuffy feeling. It cause suffocation when its concentration becomes 8 to 10% even in the presence of sufficient oxygen causing dizziness, headache visual and hearing dysfunction and also cause unconsciousness within few minutes to an hour. Therefore, it is necessary to tackle the issue concerning human health and environmental pollution.

Introduction

In 1640, the Flemish chemist Jan Baptist van Helmont burned charcoal in a closed vessel and observed that the mass of the product was much less than that of the original charcoal.[1] And he interrelated that the remaining charcoal had been changed into an invisible species known as `gas' or "wild spirit".[1,2] Later in 1750s , the Scottish physician named Joseph Black studied the properties of carbon dioxide. He observed that when lime stone was heated with acids, it yield a gas which he called 'fixed air' and he also observed that when this fixed air was denser than air and it neither support flame nor animal life. Black used the phenomenon, that when this fixed air was bubbled through lime water, it would precipitate calcium carbonated to illustrate that CO_2 gas is produced by microbial fermentation and also by animal respiration. An English chemist Joseph Priestlry, in 1772, published a paper whose title was "Impregnating water with fixed air'' in which he explained an experiment of dripping 'oil of vitrol' onto chalk in order to produce CO_2. The gas was forced to dissolve by agitating a bowl of water in contact with the gas. Carbon dioxide was the first gas which was described as a discrete substance and it was also

liquefied by Michal Faraday and Humphry Dary in 1823.[3] In 1835, the French inventor Adrien-Jean – Pierre Thilorier, find out that while opening a pressurized container of liquid carbon dioxide the cooling produced by the rapid evaporation of the liquid results a 'snow' of solid CO_2 known as 'dry ice'.

Carbon dioxide is a colorless and odourless gas at normally low concentrations with a density of about 60% which was greater than that of dry air. [1] It occurs as trace gas in the atmosphere and its current concentration is approximately 0.06% by volume which have risen from pre-industrial levels of 300 ppm approximately. [2] Carbon dioxide is produced by metabolism of carbohydrate and lipids which produce energy through respiration in aerobic organism. CO_2 is also produce by the decomposition of organic matter and by fermentation of sugars in wine, beer, bread making. Carbon dioxide is also produced by burning of fossil fuels like coal, petroleum, natural gas etc. and wood. CO_2 is an unwanted waste product in many oxidation processes like in the formation of acrylic acid over 6 million tons per year. [3] Carbon dioxide is added to carbonated beverages and drinking water to add effervescence. Dry ice is used as refrigerant and it is also used as an abrasive in solid co_2blasting. It is versatile industrial material which is also used as a fire extinguisher.[4] Due to increase in industrial revolution and deforestation, it is the most important long lived greenhouse gas in Earth`s atmosphere, which lead to global warming.[5] It react or dissolved in water to from carbonic acid which leads to ocean acidification. Deforestation, Industrial Revolution have increased the concentration of carbon dioxide that's leads to global warming. It is soluble in water to form carbonic acid [weak acid]. CO2 is an unrecovered waste product on industrial scale, which is produced by several Methods. It can also be obtained by distillation from air, but this method is in efficient. The burning of Carbon-based fuels produces carbon dioxide. Depletion of fossil fuels, anthropogenic climate change, and high risk of nuclear power generation lead to an increasing interest in future energy based on renewable and regenerative sources.[6,7] Thermochemical route such as CO_2 hydrogenation and photocatalysis are found to be a very promising opportunity for CO_2 utilization.[8-12] In this project, this review article focuses on the modification and development of nanostructured porous catalysts especially cupper based and nickel based for CO_2 utilization to fuels and chemicals such as methanol and formic acid. The conversion of Carbon dioxide via hydrogenation route into formic acid or formate is a valuable basic chemical and a promising energy storage material and has received a great deal of attention. But hydrogenation of CO_2 has various limitations such as high cost of hydrogen consumption and synthesis of low cost non-noble transition metal catalysts. The transition metal complexes, can provide higher CO_2 conversion efficiency due to their binding ability with CO_2 and higher visible light absorption [13,14]. The metal complexes due to their homogeneous nature limits their applicability for practical applications because of slow recovery and non-recycling. To end the issue, an ideal approach has been considered for immobilization or transfer of metal complexes to semiconductor, that provide not only recyclability of photocatalyst/facile recovery, but also the binding capacity of metal centre rises the CO_2 availability for higher conversion efficiency on the surface. [14-17]. Carbon dioxide has also been converted into many useful products like Methanol, Formic acid, Carboxylic acid, Polymers, Hydrocarbons, Methane, and Many more. Researchers have been aware of the economic and environmental benefits of using carbon dioxide as a feedstock for the formation of useful products for decades. It is the generally inexpensive waste product, which contributes to global warming. A large amount of fundamental research has been formed regarding carbon dioxide conversion. The important challenge for converting carbon dioxide waste streams into useful products is to develop processes and design of efficient nanomaterials that utilize less amount of non-renewable energy, are economically competitive, and provide us the substantial decrease in emission of greenhouse gases to existing technology.[17] This technology is very important for researchers because it will be extremely needed for the efficient reduction of carbon dioxide in the upcoming future. Recent research focused on the nano-based composite materials for the conversion of CO_2 to methanol and formic acid. Our goal is to develop

nanoparticles and convert the carbon dioxide into useful fuels and chemicals by utilizing the synthesized nanoparticles. There are many methods for the synthesis of nanomaterial, but the most used methods are hydrothermal and wet impregnation method. The nanomaterials which are synthesized are discussed in the summary itself. We focused on the synthesis and characterization of mesoporous copper and nickel nanomaterial for the conversion of carbon dioxide to methanol. We also studied the reported cupper based nanomaterial and nickel nanomaterial and its photo catalytic application for methanol synthesis. The thesis showed the yield of methanol production via photo catalytically using Cu-based nanomaterial. More over carbon dioxide technologies are also well defined for CO_2 conversion. This review has mainly focused on the recent advancement in fabrication, characterization and application of low cost nanomaterial such as mesoporous Ni-based and porous Cu-based nanocomposites. It also elucidate the most advance trend for the production of low cost transition porous nanomaterials as semiconductor for the photocatalytic reduction of CO2 to methanol under visible light. The most important factor is to change the photocatalytic activity and to simplify separation process which initiate a magnetic compound over magnetic nanocomposites or nanosheets. The effects on the structure, physico-chemical properties, photocatalytic activity towards conversion of CO_2, hydrogen generation, and supercapacitors are also discussed in detail. The most valuable approach is the reduction of CO_2 into solar fuels by photolytic method to address the environment and transportation fuel. CO_2 reduction into useful products is possible but the more valuable product is methanol which is considered as transportation fuel due to its high energy content. Because of its liquid nature, it can be easily stored and transported. I contributed the successful synthesis of an inorganic nanocomposite porous CuO and porous NiO nanomaterials using neem leaf extract for the photocatalytic reduction of carbon dioxide to methanol under visible illumination. The synthesised photocatalyst exhibited a remarkable enhancement in the yield of methanol as compared to the other reported semiconductor for CO_2 reduction under identical conditions.

Conversion of CO_2 into Fuels and Chemicals by Emerging Technologies:-

1. Methane production:-

Methane is predominantly obtained rarely on industrial scale from natural gas. CO_2 is hydrogenated to methane from Sabatier reaction. Methane is also produced using N-doped catalyst by electrochemical reductions with reported faradic efficiencies in the range of 80-94% in H-cells or standard three electrode. Methane is used to make water gas and is used as fuel.

2. Carbon Monoxide Production:-

Carbon monoxide is fromed from carbon dioxide through endothermic water gas shift reaction in which CO and H_2O are produced from CO_2 and H_2, using heterogeneous catalyst. A range of heterogeneous catalysts have been used for the reverse water gas shift reaction.

Now a days, there are no catalyst for the direct thermo chemical reduction of CO_2 to CO and O_2. Solid oxide electrolysis cell [$SOEC_S$] in high temperature and solutions phase are gas diffusion electrolysis cell in low temperature performed a reaction of direct electrochemical splitting of CO_2, CO and O_2 which provide an alternative to the convention fossil fuel.

3. Methanol production:-

Methanol is produced from syn gas, obtained from fossil fuel and is synthesized globally on a scale of approximately 70million tons in 2015. The mechanism of methanol production involved initial conversion of carbon monoxide and water to CO_2 and H_2 via water gas shift reaction. If large amount of

H2 is available, then it represents an opportunity to utilize waste CO_2 that is obtained during syngas production and this could improve current technology and increase plant efficiency.

Various catalysts and reactors have been developed by researchers for direct hydro-generation of CO_2 to CH_3OH. About 100 tons of Methanol is produced by Mitsui chemical company per year from CO_2. Secondly, approximately 200 tons of Methanol is produced from CO_2 by carbon recycling international, located in Iceland per year. Second, Carbon Recycling International located in Iceland, produces approximately 4500 tons of Methanol from carbon dioxide each year. The plant uses geothermal and hydro energy for methanol production. The plant use hydro and geothermal energy for H2 production and uses CO_2 captured from the fuel gas of geothermal power plant.

Catalysts are required if direct hydro generation of CO_2 to methanol is to replace methanol production for water gas. Now, research is ongoing from electrochemical reduction of carbon dioxide to CH_3OH in which protons and electrons are used as H_2 source. Recently it was reported that with faradaic efficiency the electro catalyst i.e Mo-Bi bimetallic chalcogenide could produce methanol more than 70%.

5. <u>Hydrocarbon Production:-</u>

Carbon Monoxide and dihydrogen are converted into liquid fuels by fischer-Tropsch Process. One method for the production of fuels from carbon dioxide could involve initially electrochemical synthesizing carbon monoxide from carbon dioxide and the second step is thermally combining the carbon monoxide with dihydrogen to synthesize fuels.

The first step is the generate carbon monoxide from carbon dioxide through reverse water- gas shift reaction then, through the mechanism based on Fischer-Tropsch reaction liquid fuel is formed from carbon monoxide and dihydrogen. The photo or electroreduction of carbondioxide to chemical fuels has also attracted significant research. Most commonly C_1 feedstocks such as HCOOH, CH_3OH, CH_4 are formed from reduction of CO_2. Products containing C-C bounds are also formed in the presence of copper catalysts. Higher products and the other major challenge in electrochemical carbon dioxide reduction to fuel is inhibiting the evolution of hydrogen reaction which products H_2 as by product.

6. <u>Benzoic Acid production:-</u>

Benzoic acid is prepared by inserting CO_2 into C-H bond of benzene .Benzoic acid is a relatively small scale chemical which is used as an intermediate in phenol synthesis and in the production of preservatives and solvents. About 700,000 tons of Benzoic acid is produced per year approximately. Currently, Benzoic acid is synthesized industrially through the aerobic oxidation of toluene.

7. <u>Polymer production:-</u>

Carbon dioxide can be used for the production of polymers either through direct or indirect approach. In direct approach CO2 is used as a monomer unit and is directly converted to polymer. In the indirect approach, CO_2 is first converted into monomer which is then polymerized to form polymer.

Plastics such as polycarbonates and polyurethanes have a wide range of applications. Polycarbonates are synthesized through the reaction of phosgene with 1,2-diols.The copolymerization of CO_2 with epoxides to produce polycarbonates is an alternative synthetic route by using homogeneous and heterogeneous transition metal catalysts. Typically homogeneous catalysts are preferred because they give higher selectivity. Empower materials currently sells polyethylene carbonate made from ethylene oxide and

carbon dioxide. Economic manufactures polycarbonates that contain up to 50% CO2 by weight. Novomer and Covestro are both selling polyether carbonates for use in polyurethane synthesis. Recently research has begin on using epoxide starting materials which are derived from renewable feedstocks such as limonene oxide, cyclohexadiene etc.

8. Oxalic acid and oxalate production:-

About 120,00 tons of oxalic acid and oxlate is produced per year from CO and oxygen with alcohol. The reaction of alcohol, carbon monoxide and oxygen produce distress of oxalic acid, which upon hydrolysis with acid give oxalic acid. Researchers are in continuo work to produce oxalates and oxalic acid from CO_2 from more efficient methods.

9. Formic acid production:-
The production of Formic acid involves two steps:
[a]. Reaction of CO with Methanol to form Methyl Formate.
[b]. Conversion of Methyl formate to Formic acid, either through reaction with ammonia or through direct hydrolysis with water to produce formamide and subsequent acidification with H_2SO_4.
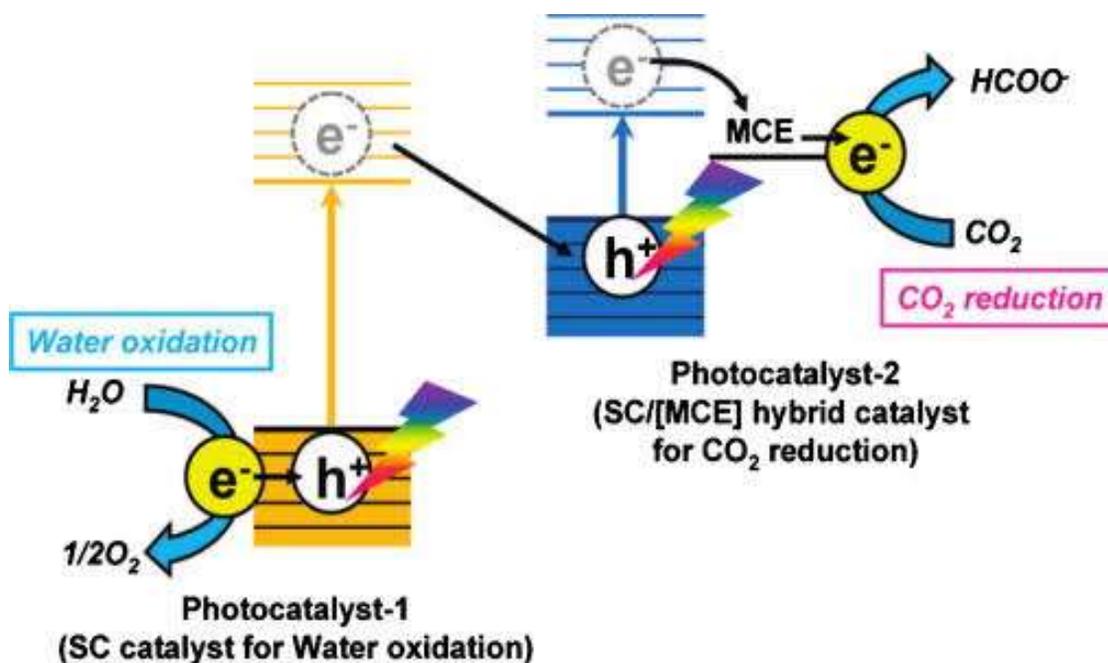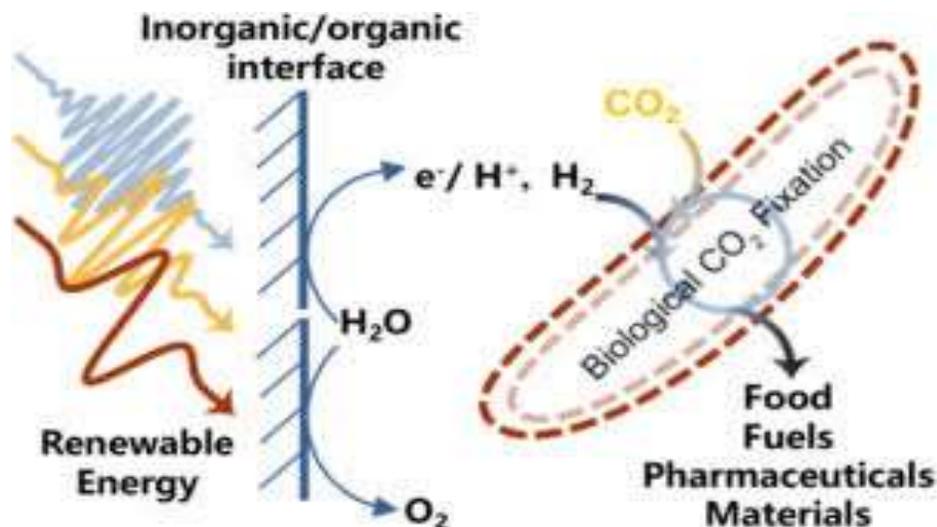

Scheme1: Photo catalytic and photo thermal catalytic conversion of CO_2
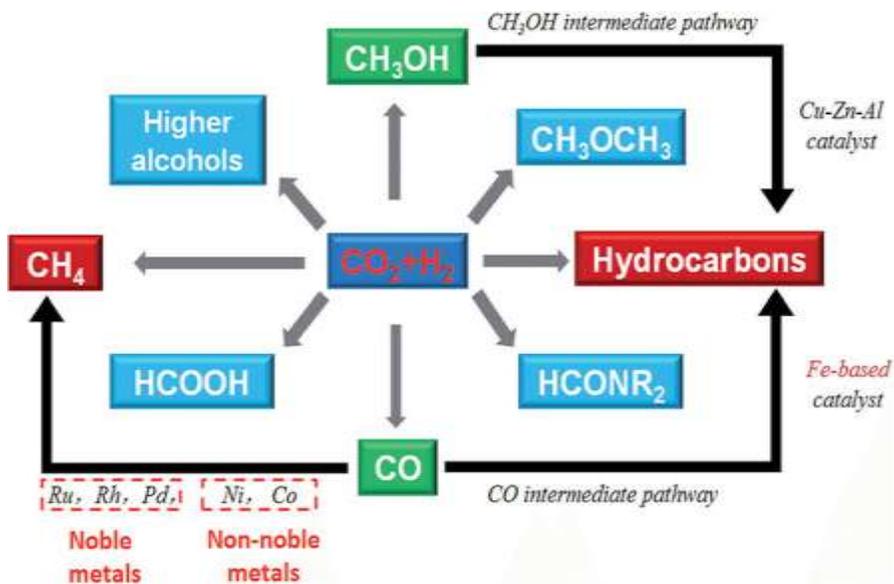
Scheme 2: Catalytic conversion of carbon dioxide[4,5].
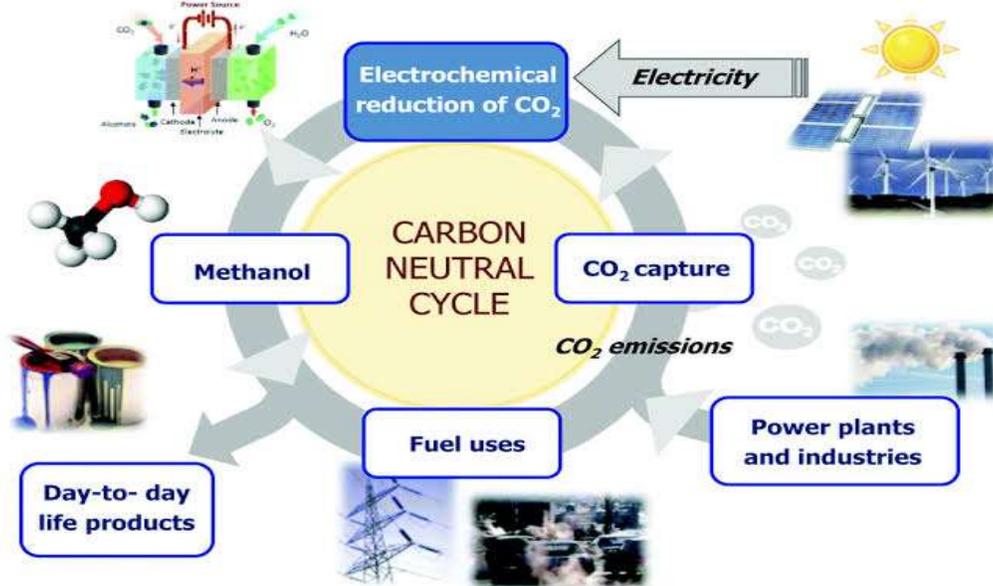
Scheme 3: Electrochemical Conversion of CO_2

Scheme 4: Bioconversion of CO_2 to useful products

Materials and Methods

All the substrates and solvents used are commercially available. Porous NiO and porous CuO was synthesised by modifying following the literature reported [11]. Deionized water was used throughout the synthetic procedures. Nickel nitrate hexahydrate, hydrazine hydrate, ethanol, and sodium hydroxide were purchased from Merck India. Organosilane octadecyl dimethyl 3-trimethoxy silyl propyl ammonium chloride (ODAC) (60 wt % in methanol) was purchased from Aldrich Chemicals. Copper salt, $Cu(NO_3)_2.6H_2O$ was purchased from Chemicals Sigma Aldrich. Neem extract was prepared in aqueous solution.

Result & Discussion

Synthesis of nanomaterials and their application in photo catalytic reactions

Methods of Synthesis of Nanomaterial:-

WET- IMPREGNATION METHOD. Nanoparticles are synthesised from wet-impregnation method. In this process, an insoluble precipitate is formed by mixing or treating various solutions of suitable compounds. The nanomaterial from this method are separated from solvent and the soluble derivatives of the reactions are the combination of sedimentation, centrifugation, evaporation, washing and filtration. The particle size is adjusted by choosing reagent concentration and solution temperature or by adding suitable inert agents that affect viscosity and diffusion rate of liquid. Alternatively, if the particle deposition on the surface of some solid substrate take place, then the starting solutions can be coated on that surface by dipping or spin-coating and then the reaction is carried out. The suspension of nanoparticles that result from this process is an example of colloid. Importsnt example of this method is the formation of metal oxide over hydroxide nanoparticles from metal alkoxides and chlorides hydrolysis. Besides being cheap and convenient, the wet chemical approach allows fine control of the particles chemical composition. Even small quantities of dopants such as organic dyes, can be introduced in the reagent solutions end up uniformly dispersed in the final product.[8]
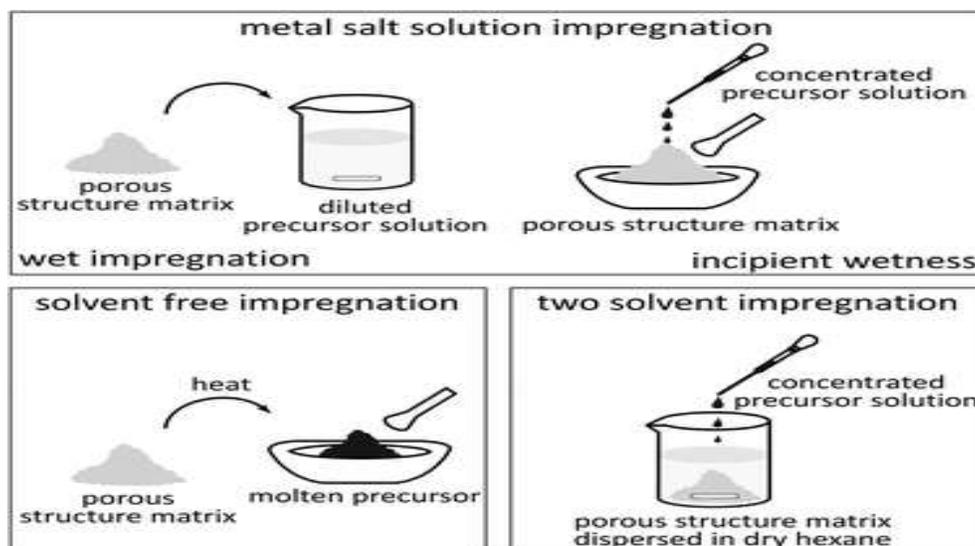
Scheme 4: Experimental view of wet-impregnation method

HYDROTHERMAL METHOD:- This method of preparation is generally the growth or synthesis of crystals under high temperature and high pressure water conditions which are insoluble at ordinary temperature and pressure.[9] Hydrothermal synthesis is usually carried out below 300 degree Celsius due to maximum value of ionic product. The critical pressure and temperature of water is 22.1MPa and 374 degree Celsius respectively. The solvent properties of many compounds change dramatically under supercritical conditions. In this method the reactants are dissolved or placed in a closed vessel and the vessel is heated above boiling point.[10] Materials which have high vapour pressure near their melting points can be produced by hydrothermal method. This method is also suitable for production of large good quality crystals while maintaining control over their composition.

Reported porous nanomaterial

1. Formation of Co_3O_4 Nanoparticles:

The formation of Co_3O_4 Nanoparticles is reorted in the literature. In this typical formation procedure, 4.3 g of Cobalt(II)chloride hexahydrate and 1 g of Urea solution was mixed with 50 ml of distilled water. The resultant solution was then placed in the autoclave and then it was waited in the furnace at 105-180°C for 5 h. It was precipitated and washed various times with distilled water and then dried at 65°C for 8 h. The particles obtained was annealed for 4h at 400°C.

2. Formation of Cu dopped TiO_2 Nanoparticles:-

2.05 g of TiO powder was dissolved in 110 ml of aqoues solution containing 12 M NaOH and 5.00 mmol $Cu(NO_3)_2.6H_2O$ was subjected to hydrothermal treatment at 150°C for 24 hrs in autoclave. $Cu(NO_3)_2.6H_2O$ was used as Cu dopant source.[12]After the completion of the reaction, the white solid precipitate was obtained and collected. The white solid was washed with 0.1 M HCL [220ml] followed by distilled water until pH 7 of washing solution was obtained. Then, the white solid was separated and subsequently dried at 80°C for 24 hrs.[12] Obtained powder was then for 2 hrs. For comparison, undopped TiO_2 nanotubes was also synthesized using similar procedure but without the presence of Cu $(NO_3)_2.6H_2O$.

3. Formation of mesoporous CuO Nanoparticles

The Cu/Cu_2O Nanoparticles was formed by modifying the method as reported in the literature. [13] In this method, 0.1M of copper (II) sulphate pentahydrate solution was added into 130 ml of 1.2% starch solution with vigorous stirring for 30 minutes. Then 50ml of 0.02 M, ascorbic acid is added with continuous rapid stirring. 0.01 g of an organosilane template, octadecyl dimethyl (3-trimethoxysilylpropyl) ammonium chloride (ODAC) is added with stirring. Subsequently, 40ml of 1M NaOH solution was slowly added to the prepared solution with constant stirring and heating to 80 °C, for about 3 hour. The solutions colour changes from yellow to ocher. After the completion of the reaction, the solution was removed from the heat and allowed to settle overnight and the supernatant solution was then discarded cautiously. The precipitates were separated by filtration from the solution and washed with de ionized water and ethanol for four times to take out excessive starch bound with the nanoparticles. Precipitates are dried at room temp.

Synthesised porous nanomaterial
4. Formation of catalyst CuO Nanomaterial:-

The mesoporous CuO nanoparticles was prepared by hydrothermal method with Sodium Hydroxide as precipitating agent [14]. Copper precursor solution was prepared in a beaker by the addition of 0.3 M $CuCl_2.2H_2O$ and 0.5 M Sodium Hydroxide dissolved in 50ml of double distilled water. 0.01 g of an organosilane template, octadecyl dimethyl (3-trimethoxysilylpropyl) ammonium chloride (ODAC) is added with stirring. The pH value of the solution was set to be 10 by the dropwise addition of aqueous solution of NaOH into the above solution under constant stirring The resultant solution was transferred to the stainless steel autoclave and hydrothermal synthesis was carried out for about 150 °C for 12h.The obtained black precipitates was washed various times with deionised water & acetone to remove impurities. The final product is dried at 70°C for 5h. [15]

5. Formation of Copper Nanoparticles:-

Mesoporous Copper was produced using modified hydrothermal method reported in literature. In this formation, 1.5 g of copper nitrate hexahydrate was dissolved in 70 mL of de-ionised water with vigorous stirring for 2.5 hrs in a beaker at 60°C. The pH of the solution was maintained at 11.5 by adding Sodium Hydroxide solution (1M) followed by the drop wise addition of 0.1 g of an organosilane template that is octadecyl dimethyl (3-trimethoxysilylpropyl) ammonium chloride (ODAC). The temperature of the solution was raised slowly up to 70°C with continuous stirring. Then, 3 mL of hydrazine hydrate (1M) was added to this solution. The final solution was then placed in autoclave at 150 °C for 1 day. The synthesised material was then washed with ethanol to remove the impurities and dried at 80°C. Finally, the dried material was calcined at 400°C with air for 4hrs. The prepared cupper nanomaterial was characterized by TEM, and TDA-DTA before photo catalytic reaction. Finally, the synthesized Cu was used for the photoreduction of CO_2 in visible light.

6. Formation of porous NiO Nanoparticle

Mesoporous NiO semiconductor was produced using modified hydrothermal method reported in literature. [11]. In this type of synthesis, 1 g of nickel nitrate hexahydrate was dissolved in 50 mL of de-ionised water with vigorous stirring for 2 hrs at 40°C in a beaker. The pH of the solution was set at 11 by adding Sodium Hydroxide solution (1M) followed by the dropwise addition of 0.1 g of an organosilane template that is octadecyl dimethyl (3-trimethoxysilylpropyl) ammonium chloride (ODAC). The

temperature of the solution rised slowly up to 60°C with continuous stirring. Then, 3 mL of hydrazine hydrate (1M) was added to this solution. 3ml solution of neem extract is then added at 70°C with continuous stirring for 30min. The balck precipitate is then formed. Finally, the dried material was calcined at 400 °C with air for 4h. Finally, the synthesised Ni/NiO nanomaterials is the tested for photoreduction of CO_2 and also used for the immobilization of Cobalt Phthalocyanine for the photoreduction of CO_2.

7. Formation of CoPc/NiO catalyst

In this synthetic process, firstly, 100 mg of Cobalt Phthalocyanine was dispersed in 10 mL ethanol for 2 h with continous vigorous stirring at room temperature in a beaker. 1 g of Ni/NiO was added to another beake in 10 mL of deionised water with sonication for 2 hrs to rise the hydroxyl functionalities. Afterwards, the colloidal solution of Cobalt Phthalocyanine was dispersed into the Ni/NiO solution with overnight stirring or until the complete evaporation of the solvent. The residue so obtained was thoroughly washed with ethanol and dried under reduced pressure at 60°C. The yield of the composite Cobalt Phthalocyanine/NiO was found to be 1.05 g.[11]

Methodology of Experiments: The material Cu-based material was synthesised based on the modification of previous report. The Ni-based mesoporous Ni-based nanomateraials also synthesised on modification of reported method in literature. The photocatalytic conversion of CO_2 to methanol was studied over Cu-based and Ni-based nanomaterial in visible light. The synthesised nanomaterial were then tested for photocatalytic CO2 mitigation. The methodology used in this experiment of photolytic conversion was performed in a cylindrical vessel of volume 60 ml which had a diameter of 5 to 8 cm using a 20-Watt LED bulb as a visible light source under continuous stirring. Then, the product was analyzed by Gas chromatography.
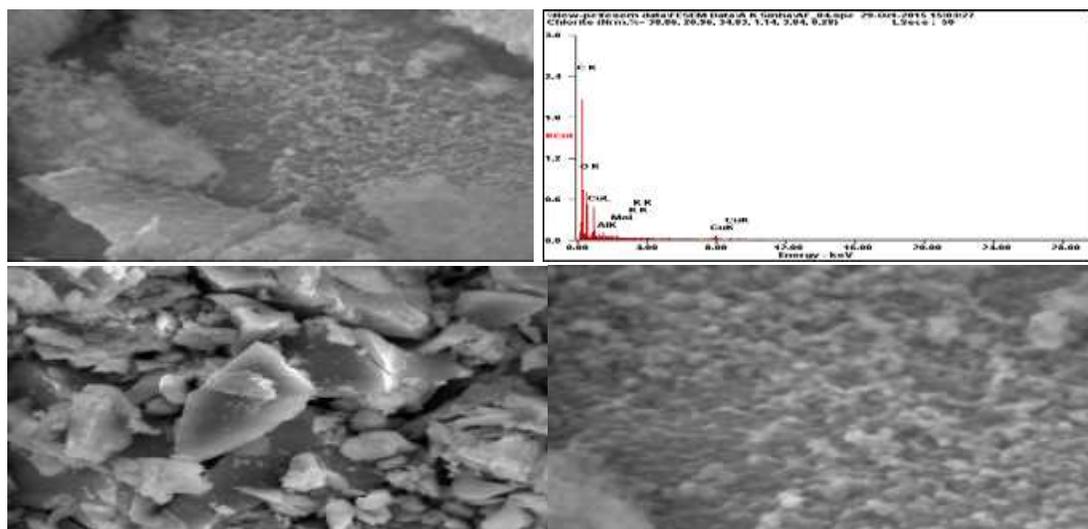

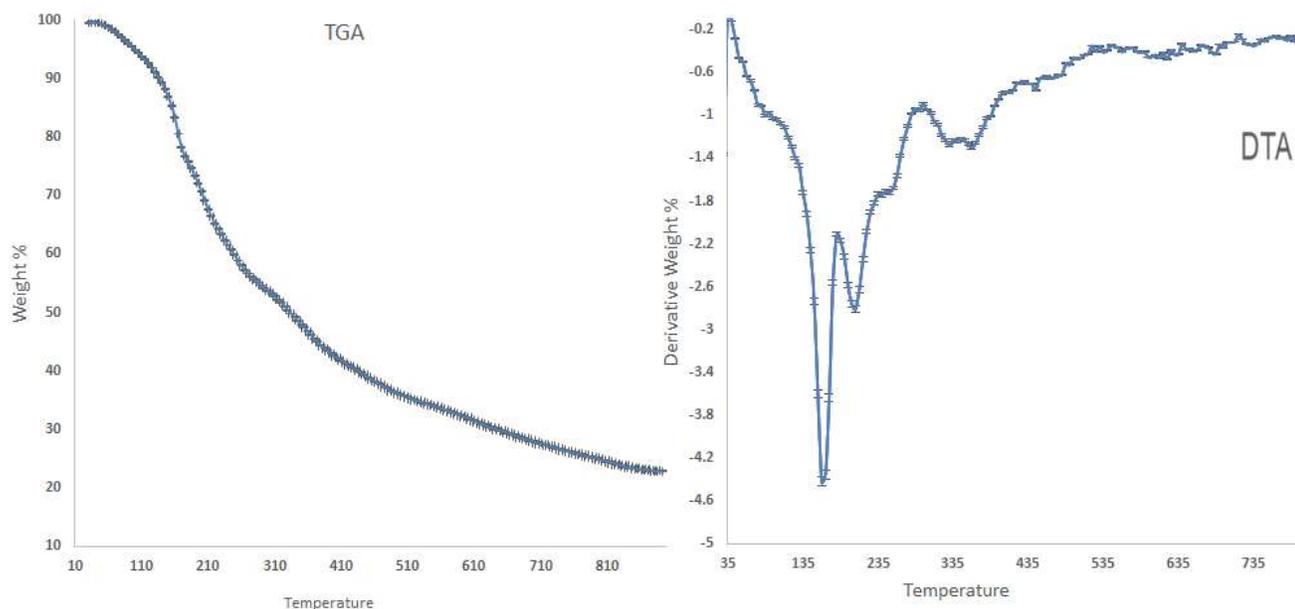Fig 2: TEM and EDAX analysis of synthesised porous CuO nanomaterials.

Fig 3: TGA and DTA analysis of synthesized Cu nanoparticle to show the thermal stability of material.

The above graphs show that the thermal properties of as prepared Copper nanoparticles were investigated by thermogravimetric analysis [TGA] and differential thermal analysis [DTA] as shown in above fig. The initial weight loss of 45% in the TGA curve up to 210°C, accompanied by an endothermic peak at 170°C in DTA, is assigned to the loss of free and coordinated water molecules present in the sample. The future changes in the weight (15%) in the temperature range of 220-570 °C in the TGA curve is due to loss of capping agent. It should be noted that the at last there will be no change in TGA curve which indicates the production of stable Cu nanoparticles.
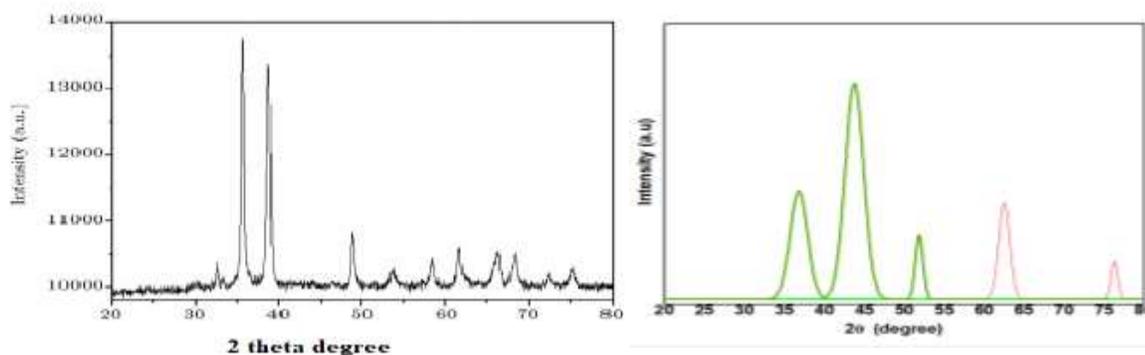

Fig. 4: XRD spectrum of synthesised porous Cu nanoparticle and porous Ni nanoparticle.[11]

The XRD pattern of the sample shown in Figure 4a. Diffraction peaks are observed those of pure face-centered cubic (FCC.) Cu (JCPDS, File No. 04-0836), corresponding tothe (111), (200), and (220) planes. The crystallite size can be found by applying Sherrer's equation and the average crystallite size is found to be 11 nm. The observation of diffraction peaks Are intense and sharp for the Cu nanoparticles

indicates that these are crystalline in nature. The unreduced Ni/NiO catalyst shows the five peak at 2θ of 36°, 44°, 54°, and 76°, which are attributed to NiO (111), Ni (111), NiO (200), NiO (220), and Ni (220), respectively(figure 4b).[11]

Table 1 describes the production of methanol through the photo catalytically and via hydrogenation route for the conversion of carbon dioxide. The hysdorgenation of carbon dioxide yields maximum conversion of CO2 and maximum methanol yield (34000 μ mol) using Ni-based nanomaterial (Ni-InAl/SiO2) whereas 17000 μ mol methanol yield using Cu-based nanomaterial (Cu/ZnO/Al2O3).We studied the photocatalytic conversion of CO2 using synthesised porous NiO and porous CuO yielded 35 μ mol and 400 μ mol of methanol with sustainable route.

Table. 1. Photocatalytic conversion of CO_2 using different reported Cu-based nanomaterials

Photocatalyst/materials	Method /Light	Conditions	Yield /Selectivity	Reference
Blank	Visible	Cylindrical vessel at room temp with LED light	-	11
Cu/CuO	Visible	Cylindrical vessel at room temp with LED light	Methanol 93μ mol	My work
Porous NiO	Visible	Cylindrical vessel at room temp with LED light	Methanol 35μ mol	My work
Cobaltphthalocyanine	Visible	Cylindrical vessel at room temp with LED light	Methanol 43μ mol	11
Cobaltphthalocyanine /NiO	Visible	Cylindrical vessel at room temp with LED light	Methanol 315μ mol	11
Porous CuO	Visible	Cylindrical vessel at room temp with LED light	Methanol 400μ mol	My work
Cu dopped TiO_2	Visible	Cylindrical vessel at room temp with LED light	Methanol 110μ mol	14, 17
Cu/ZnO	Hydrogenation	Fixed bed reactor at 250 C & 20 bar H2	Methanol selectivity24%	7
Cu/ZnO/Al2O3	Hydrogenation	Fixed bed reactor at 250 C& 20 bar H2	Methanol 17000 μ mol	17
Ni-InAl/SiO	Hydrogenation	Fixed bed reactor at 250 C& 20 bar H2	Methanol 31000 μ mol	17

Table 2: Physical properties of synthesized porous metal nanoparticles

Nanomaterial	Surface area(m^2/g)	Pore diameter (nm)	Pore volume(cm^3/g)
Mesoporous Ni/NiO	250	3.5	0.16
Mesoporous green NiO	180	3.1	0.18
Porous CuO	60	2.1	0.08

Table 2 shows the physical properties of synthesized porous copper and nickel nanomaterial. The mesoporous Ni/NiO nanomaterial reported high surface area 250 m^2/g and pore diameter 3.5 nm and pore volume is 0.16 cm^3/g. We have synthesized the Cu and Ni nanomaterial by green route of synthesis using water as solvent and neem extract as reducing agent. The synthesized porous green NiO has surface area 180 m^2/g and pore diameter is 3.1 nm and pore volume 0.18 cm^3/g. The synthesized porous cupper nanomaterial has 60 m^2/g and pore diameter 2.1 nm and pore volume is 0.08 cm^3/g. These properties of synthesized porous copper and nickel nanomaterial can also be seen in the TEM images.
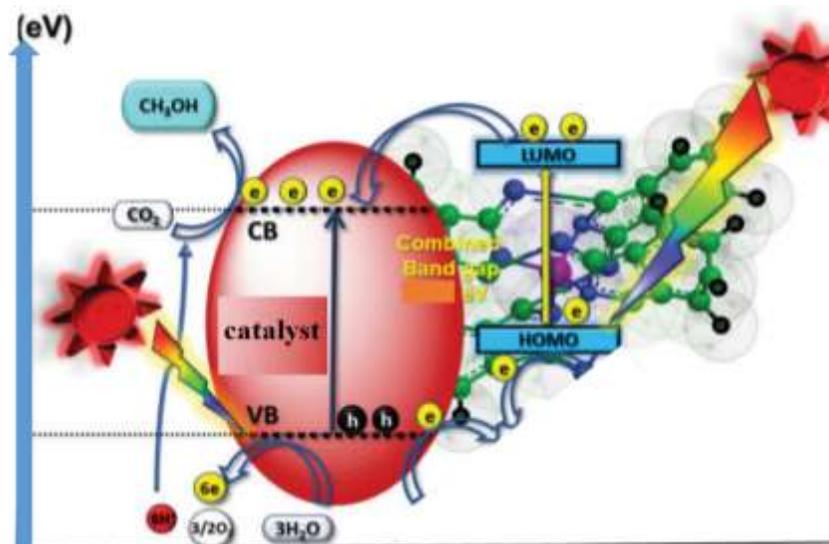

Fig4: Mechanism scheme for photocatalytic conversion of CO_2 to platform chemicals such as methanol.[11]
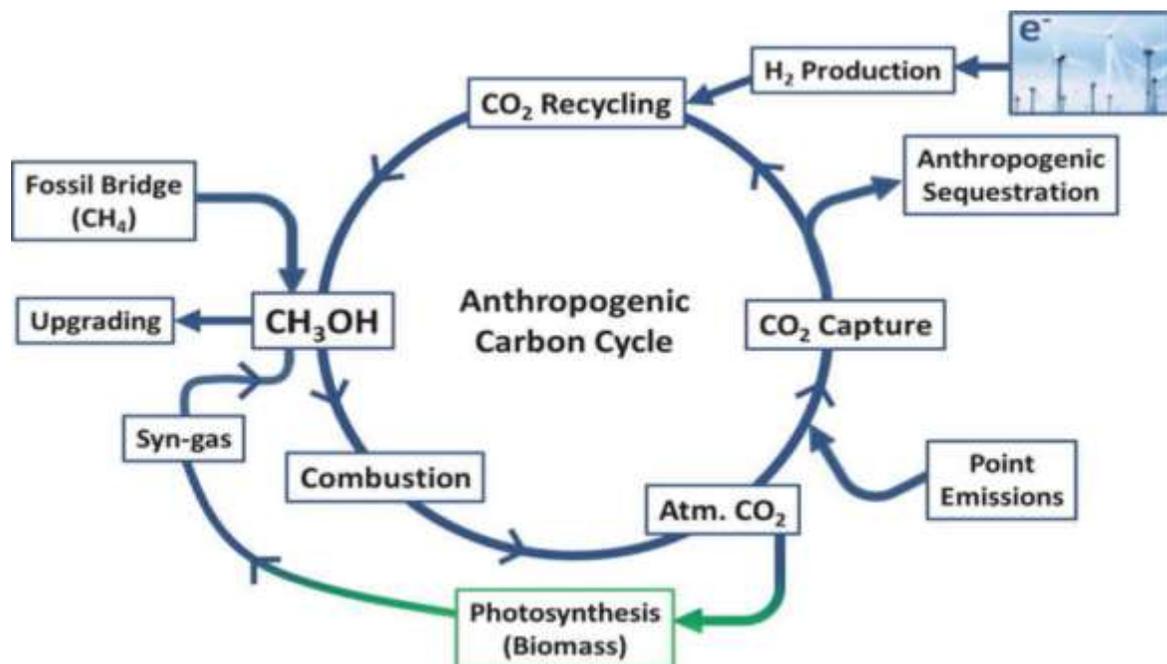
Fig 5: Cycle for Methanol formation from carbon dioxide.

Catalysts + hv ⟶ catalyst (eCB- + hVB+)

H20 + hVB+ ⟶ 1/2O2 + 2H+

CO2 (aq) + 2H+ +2eCB- ⟶ HCOOH

HCOOH + 2H+ ⟶ HCHO + H2O

HCHO + 2H+ ⟶ CH3OH

Scheme 5: CO_2 reduction pathways and mechanism by photocatalytic reaction.

Concluding remark

The articles shows various approaches have been implemented for the development of both homogeneous and heterogeneous catalysts for photocatalytic conversion of CO_2 to useful chemicals such as methanol and formic acid. This work systematically demonstrates the synthesis of Cu-based and Ni-based Nanomaterial from hydrothermal and wet impregnation method. The applications of nanomaterial studied for the carbon dioxide conversion into useful chemicals and fuels in visible light. TEM analysis shows the posous morphology and structure of cupper nanoparticles. The TGA and DTA results show thermal stability of cupper and Ni-based nanomaterials. XRD results show the crystalline nature of synthesised porous NiO and CuO nanomaterials. The results from Gas chromatography showed the yield of methanol production via photocatalyic route using cupper-based nanomaterial. Plausible mechanism for the photocatalystic conversion of CO2 to methanol is also described.

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