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USE OF GRAPHITIC CARBON NITRIDE – CDS – $BIVO_4$ COMPOSITE FOR PHOTOCATALYTIC REDUCTION OF SODIUM CARBONATE TO FORMIC ACID

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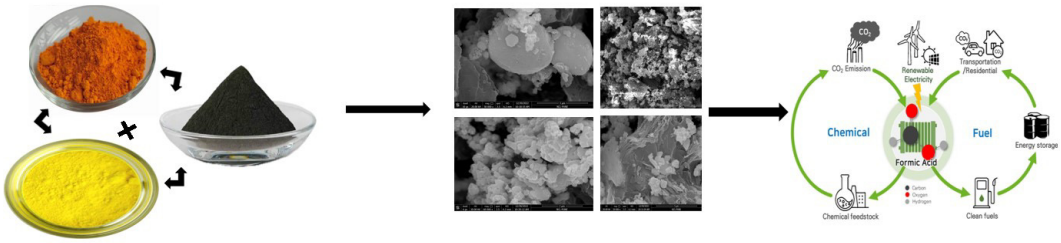
Abstract: The conversion of CO_2 into valuable chemicals and fuels serves as a promising route for mitigating the greenhouse effect of CO_2 and meeting energy demands. The carbon atom in CO_2 molecule exhibits the highest oxidation state and CO_2 itself with the C–O bond strength of 364 kJ/mol is chemically stable, so it is difficult to be activated and requires a large amount of energy to undergo conversion. In general, the reduction of CO_2 can be carried out by chemical methods, including catalyzed hydrogenation reduction, photocatalytic reduction, thermochemical reduction, electrochemical reduction etc. Influenced by "artificial photosynthesis", different energy mimetic fuels such as formic acid, methane, etc. can be prepared by the reduction of carbon dioxide captured from the atmosphere while maintaining different reaction strategies, such as photocatalysis, and photo electrocatalysis. Graphitic carbon nitride (g-C_3N_4) has been recognized as a highly potent photo- as well as electrocatalyst for the CO_2 reduction reaction (CRR), primarily due to its high chemical and thermal stability, low toxicity, cost-effectiveness, visible light absorption capacity, and ingeniously tunable synthetic routes as compared to other semiconductor platforms.

Graphical Abstract



INTRODUCTION

The overconsumption of fossil fuels by a rapidly growing economy releases a large amount of CO_2 into the atmosphere. Among the various heat-trapping gases, CO_2 predominantly increases the Earth's temperature leading to global warming. There have been increased efforts to control and scavenge the greenhouse gases from the atmosphere. Among various technologies adopted, consumption of CO_2 as a valuable chemical feedstock, photocatalytic reduction of CO_2, is more futuristic as it requires ambient natural conditions and responds mutually to global warming and energy crisis issues. The photocatalytic reduction of CO_2 with water molecules is highly beneficial in dual terms as it converts inexpensive, abundant, and harmful carbon sources like CO_2 to high energy fuels. The readily available solar energy makes the process of reduction of CO_2 economically viable.

Tamaki *et al.* (2015) used, 1, 3-dimethyl-2-(*o*-hydroxyphenyl)-2, 3-dihydro-1*H*-benzo[*d*]imidazole

as sacrificial electron donor for photocatalytic reduction of CO_2 to formic acid. They used Ru(II)–Ru(II) supramolecular photocatalysts for this purpose. It was reported that durability, efficiency, and rate of photocatalysis are significantly increased (Φ_{HCOOH} = 0.46, TON_{HCOOH} = 2766, TOF_{HCOOH} = 44.9 min^{-1}) as compared to 1, 3-dimethyl-2-phenyl-2, 3-dihydro-1*H*-benzo[*d*]imidazole or 1-benzyl-1,4-dihydronicotinamide electron donor .

Kamada *et al.* (2020) developed a highly efficient tetradentate PNNP-type Mes-IrPCY2, for photocatalytic reduction of carbon dioxide. It was reported that formic acid was produced with 87% selectivity along with carbon monoxide with turnover number of 2560. The Mes-IrPCY2 displayed excellent photocatalytic activity for CO_2 reduction The 1, 3-dimethyl-2-phenyl-2, 3-dihydro-1H-benzo[d]imidazole (BIH) was used as sacrificial electron donor in CO_2-saturated N, N-dimethylacetamide under visible light irradiation with. It was observed that 49% quantum yield could be achieved for this reduction.

Nakada *at el*. (2015) investigated that Ru (II)–Re(I) binuclear complex (RuReCl), Ru(II) can act as photosensitizer and and Re(I) as catalyst. These were connected with a bridging ligand. Here, ascorbate has been used as an electron donor. The photocatalytic reaction produced formic acid as the main product in aqueous solution. It was reported that selectivity and turnover number of the formic acid production were 83 and 25% respectively. However, about 0.2% quantum yield of the formic acid formation was there which was much lower.

Yin *et al*. (2017) synthesized a copper-and-zinc (Cu–Zn) alloy for photocatalysis to selectively reduce carbon dioxide to formic acid. It was reported that Cu_5Zn_8 catalyst exhibited significant electrochemical reduction of CO_2. They constructed a photoelectron chemical (PEC) three-electrode system, using Cu_5Zn_8 film as cathode for CO_2 reduction in the dark and strontium titanate served as photoanode for oxidation of water. It was a observed that this PEC system selectively reduced CO_2 to formic acid with a Faradaic efficiency of 79.11% in presence of UV-light. It was also revealed that $SrTiO_3$ particles decorated Cu–Zn alloy was useful for photocatalytical reduction of carbon dioxide to formic acid under UV-irradiation. Isotope trace analysis demonstrated that water served as the electron donor to produce oxygen and organic molecules in presence of UV light, similar to photosynthesis in plants.

Zhao *et al*. (2021) fabricated that photovoltaic-photoelectrochemical cell, which can effectively produce formic acid from reduction of CO_2. They synthesized BiOI–Bi (BOI–Bi) cathode and coupled it with an argon-treated TiO_2 (TiO_2-Ar) (single crystalline) photoanode. It was reported that this exhibited high product selectivity, and good durability with excellent activity. They could obtain solar-to-formic acid selectivity of 96.5% with formic acid yield of 108.2 mmol $g^{''1}$ $h^{''1}$ under AM1.5G. It was also revealed that it can operate stably for about 12 h. it was also revealed that a photon quantum efficiency of 7.5% and a solar-to-chemical conversion efficiency (çSCC) of 8.3% could be obtained.

Kumar *et al*. (2018) developed graphene oxide modified with cobalt metallated aminoporphyrin (GO-Co-ATPP) and used it as a photcatalyst for conversion of CO_2 to formic acid in presence of visible light. It was reported that efficiency of formation of formic acid from CO_2 was 96.49 μmol in 2/h.

Zhou *et al*. (2018) studied CO_2 reduction to formic acid using ternary metal chalcogenides ((Mo–Bi)Sx/Meso CdS) as photocatalysts. It was found that the (Mo–Bi)Sx supported on mesoporous CdS was effective as well as selective for photocatalytic reduction of CO_2 to HCOOH using mixed solvent 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4)–acetonitrile) under visible light. Formic acid was the only carbonaceous product while hydrogen was only byproduct. It was reported that the rate of formation of HCOOH could reach 208 $\mu mol \cdot g^{-1} \cdot h^{-1}$ with a 72% Faradaic efficiency.

Pan *et al*. (2018) tested some ZnO nanostructures for photochemical reduction of bicarbonate to formic acid, The different ZnO morphologies studied included micron- belts, flowers, rods, and wires. They campared photocatalytic efficiency of as - the synthesized ZnO with commercial micron- and nanoparticulate ZnO, and it was found to have similar efficiency. It was reported that ZnO flowers had largest surface area of 12.9 m^2g^{-1}, and these were found to be the most efficient. They could obtain an apparent quantum efficiency (AQE) (10.04 ± 0.09%), with a better performance over commercial TiO_2 (P25).

Jiang *et al*. (2018) reported N-Fe_2O_3/TiO_2 catalyst and used for CO_2 reduction to formic acid. This proposed method enabled better electron transfer and formation of target products (formic acid and ethanol). It was reported that maximal rate of formic

acid production obtained was 74896.13 nmol h^{-1} cm^{-2} with an excellent selectivity (99.89%) under optimal condition.

Rosas-Hernández *et al.* (2015) developed RuII bipyridine (catalyst) a photocatalytic system consisting of and Ir-based photosensitizer and used it for selective reduction of CO_2 to formic acid. Triethanolamine was used electron donor. It was reported that catalyst turnover numbers up to 526 and a selectivity of 80% were formed towards formic acid. The reaction was carried out with $[Ir(ppy)_2(bpy)]PF_6$ where (ppy = 2-(pyridine-2-yl) benzene-1-ide, and bpy = 2,22-bipyridine) (photosensitizers) and $[Ru(bpy)_2(Cl)(CO)]PF6$ (catalyst) under visible light irradiation. It was observed that this photocatalytic system also exhibited activity for the photoreduction of sodium carbonate to formic acid. It was also revealed that there is a positive influence of Co (carbonyl) ligands coordinated to the metal center in different ruthenium (II) catalysts.

Du *et al*. (2018) synthesized Bi- and Y-codoped TiO_2 photocatalysts via a sol-gel method and used for photocatalytic reduction of CO_2 to formic acid in presence of visible light irradiation. It was reported that surface area of TiO_2 was increased from 5.4 to 93.1 m^2g^{-1} when the mole fractions of doping Bi and Y were 1.0 and 0.5%, respectively. Oxygen vacancies on the surface of the photocatalysts were formed may be due to doping. As a result, electron capture centers are increased and recombination of photo-induced electron and hole was there. It was observed that HCOOH yield in this photocatalytic reduction was 747.82 ìmol^{-1}g cat on using 1% Bi-0.5% Y-TiO_2 as a photocatalyst, which was 1.17 and 2.23 times higher than that with 1% Bi-TiO_2, and TiO_2, respectively.

Experimental section

The graphitic carbon nitrate (g-C_3N_4) and cadmium sulphide were purchased from the Nano Research Lab India, and ASES Works India.

Synthesis of $BiVO_4$

Bismuth vanadate powder was synthesized by a chemical precipitation method. Bismuth nitrate pentahydrate was initially dissolved in conc. HNO_3 and mixed with 0.1 M ammonium metavanadate solution. It was stirred continuously at room temperature until a clear yellow solution was obtained. This solution was treated with ammonium hydrogen carbonate to induce precipitation. The precipitate formed was filtered and washed several times with distilled water. It was then dried in oven at 60 °C overnight. It was ground and sieved followed by calcinations in air flow for 4 h at 450 °C to obtain yellow crystalline powder of bismuth vanadate.

Synthesis of ternary composite g-C_3N_4– CdS – $BiVO_4$

The g-C_3N_4, CdS and $BiVO_4$ were mixed in 1:1:1 ratio (in g) and ground in mortar with pestle.

Characterization of composite

XRD Analysis

X-ray diffraction (XRD) patterns of the g-C_3N_4 – CdS – $BiVO_4$ sample was obtained with D8 QUEST (Bruker) using Cu Ka (λ = 1.5418 Å). X-ray diffraction pattern is given in Figure 1.The XRD patterns of this composite indicated that it is crystalline in nature as sharp peaks are present in XRD spectrum.

The average size of these particles was

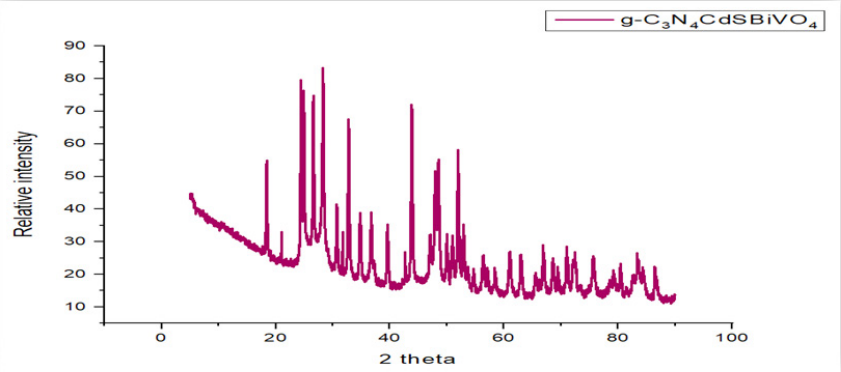


Fig. 1. XRD Pattern of composite

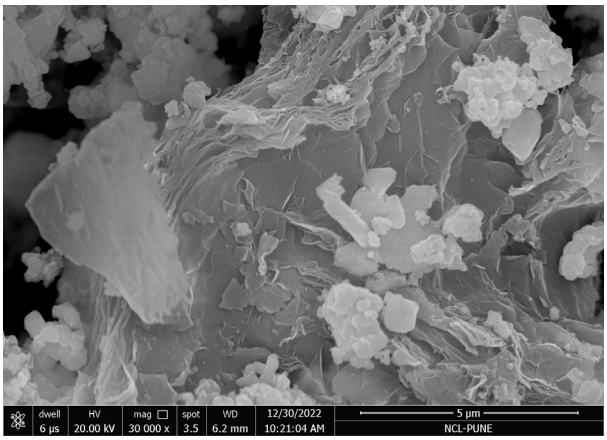
determined using Debye–Scherrer equation.D = (kë/â cos è) Where,

D = Crystalline size, K is the Scherer constant (K = 0.94), ë is the X-ray wavelength (1.54178Å) and â is full width at half maximum (FWHM). And è is Bragg's angle.

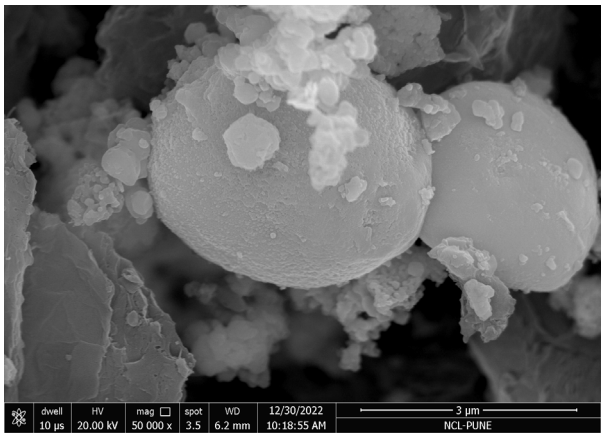
The average particle size of the sample was found to be is 91.66 nm, which is in the range of nanoparticle size.

FESEM Analysis

The morphology of g-C_3N_4,- CdS, - $BiVO_4$ was investigated by FESEM (JSM7600F, Jeol (Fig. 2). It is clear from figure that it contains flakes along with Mushroom shape.



(a) Flakes of composite



(b) Mushroom shape of composite

Fig. 2. FESEM Images of g-C_3N_4 – CdS, – $BiVO_4$

Energy Dispersive X-Ray Analysis

The element composition was confirmed through an energy–dispersive X-ray Spectrum Oxford INCA Energy 250 EDS) The EDS of composite indicates that it contains only C, N, S, Cd, Bi, V, and O. Hence the sample is pure enough. The EDS spectrum of g-C_3N_4 – CdS – $BiVO_4$ is given in Fig. 3 and data are presented in Table 1.

Table 1. EDX data of composite

Element	Wt (%)	At (%)
C	49.34	62.92
N	18.71	20.46
O	12.01	11.50
S	06.11	02.92
Cd	11.85	01.61
V	01.98	00.59

Photocatalytic experiment

Prepared a 40 ml solution of sodium carbonate 0.1325 g concentration in a flask. Fill a burette with a standard solution of sodium hydroxide (NaOH) of N/100 concentration. Added few drops of Phenolphthalein indicator to the formic acid solution, which changed from colourless to pink. Slowly added the sodium hydroxide solution from the burette into the flask containing solution, swirling gently to mix. The indicator will change colour as the pH increases. Initially, the solution will be acidic and the indicator colourless. As the approach endpoint, a faint pink colour will appear, indicating near neutralization. Continue adding the base drop by drop while swirling until the pink colour persisted for at least 30 seconds. This indicates that all the formic acid has reacted with the base, and the solution is neutral. It was observed that the photo reduction of CO_2 to formic acid was reaction in order to evaluate the photocatalytic capabilities of the g-C_3N_4, CdS and $BiVO_4$ composites. Different samples collected at different time intervals and the generation of formic acid (HCOOH) was monitored using acid – base titration method with different time fractions. For titration 2.0 ml test solution in conical flask with 2-3 drop phenolphthalein indicator than titrate with pre-standardized 0.01 N sodium hydroxide solution.

RESULTS AND DISCUSSION

These observations demonstrated that the g-C_3N_4 – CdS -$BiVO_4$ is an efcient catalyst for photocatalytic reduction of CO_2 into synthetic fuels (formic acid) for sustainable energy. Enhanced specic surface area and optical properties are usually beneficial for the activity of photocatalysts. Carbon dioxide can be

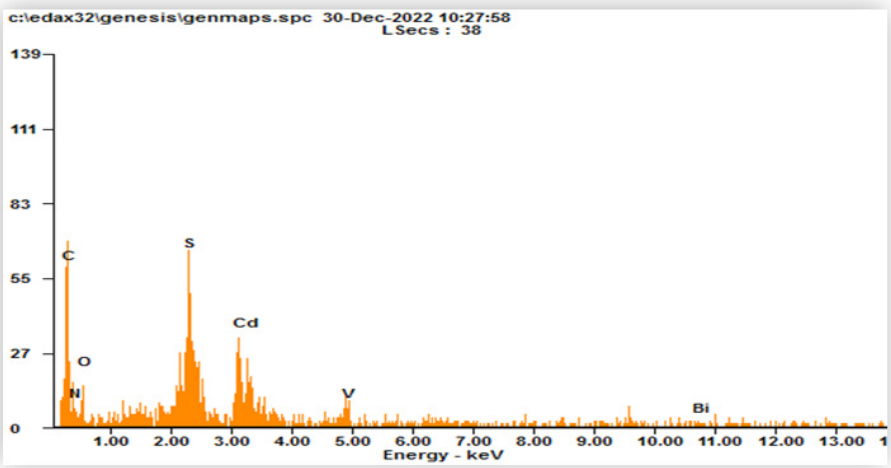


Fig. 3. EDX Spectrum of composite

trapped in the form of sodium carbonate. The sodium carbonate can be reduced to formic acid.

The effect of different parameter was observed on the formation of formic acid

Effect of pH: The effect of variation of pH was studied in the range of 7.0 – 9.0 and the results are reported in the Table 3.

Table 3. Effect of pH

$[Na_2CO_3]$ = 5.66 × 10^{-3} M Amount of composite = 0.06 g
Light intensity = 30.0 mW cm^{-2}

pH	Rate constant (k) × 104 ($^{s-1}$)
7.0	3.05
7.5	3.46
8.0	3.83
8.5	2.20
9.0	1.47

There was increase in formation of formic acid on increasing pH up to 8.0, because in alkaline range. Carbonate ions can survive. There was a decrease towards lower pH as carbonate exits as carbonic acid, which is unstable; it generates carbon dioxide and water on decomposition. There is again decreeing trend on increasing pH above 8.0. This can be explained basis on the composite that is also negatively charged due to adsorption of hydroxyl ions on its surface, this will causes repulsion between two negative species result decreasing in yield of formic acid.

Effect of Sodium carbonate concentration

The effect of concentration of sodium carbonate was observed in the range 0.9-0.17 the results are reported in Table. 4

Table 4. Effect of Sodium carbonate concentration
pH = 8.0
Amount of composite = 0.06 g
Light intensity = 30.0 mW cm^{-2}

$[Na_2CO_3]$ × 10^3 M	Rate constant (k) × 104 ($^{s-1}$)
3.40	2.22
4.15	3.01
4.95	3.69
5.66	3.83
6.42	1.98

There was a regular increase in the yield of formic acid because there are more molecules of sodium carbonate, for reduction increasing its concentration, an optimum yield was obtained 5.66 × 10^{-3} M there was a decreasing trend of formic acid yield, on increasing concentration of sodium carbonate above. This may be attributed to hindrance created by larger concentration of sodium carbonate, which restricts the approach of carbonate ions towards surface of composite As a consequence, yield of formic acid decreases.

Effect of amount of composite

The amount of composite is also likely to affect the reduction of sodium carbonate and therefore the reaction was studied in the range of 0.02 – 0.10 g. the results are reported in Table 5.

It was observed that, there was continuous increase in yield of formic acid on increasing amount of composite. This is due to corresponding increase in number of active site provided. The surface of composite of amount the maximum yield of formic acid was found at 0.06 g. Above this value,

Table 5. Effect of amount of composite
$[Na_2CO_3]$ = 5.66×10^3 M
pH = 8.0
Light intensity = 30.0 mW cm^{-2}

Composite (g)	Rate constant (k) × 104 $^{(s-1)}$
0.02	2.55
0.04	3.16
0.06	3.83
0.08	2.97
0.10	1.96

there was again a sharp decrease in the yield of formic acid, maybe due to multilayer formation of composite with no further increase in the exposed surface area. This multilayer formation support undesired electron - hole recombination

Table 6. Effect of light

$[Na_2CO_3]$ = 5.66 × 10^{-3} M
pH = 8.0
Amount of composite = 0.06 g

Light intensity (mW cm{²)	Rate constant (k) × 104 $^{(s-1)}$
20.0	3.50
30.0	3.83
40.0	2.95
50.0	2.68
60.0	2.23
70.0	1.42

There was a regular increase in yield of formic acid, till light intensity was raised 30.0 mW cm^{-2} thereafter, a decrease starts, which may be due to some side thermal reaction on increasing light intensity.

CONCLUSION

A ternary composite (g-C_3N_4 CdS-$BiVO_4$) photocatalysts with high photocatalytic activity were synthesized successfully via a simple and efficient method. The g-C_3N_4 exhibits superior performance for photocatalytic CO_2 reduction due to effective electron–hole pair separation at the composite interfaces, which in turn is based on their band positions This work has the potential to provide new insights into the development of g-C_3N_4 based composites as highly efcient photocatalysts for the conversion of CO_2 to energy rich products (formic acid) which can be used as synthetic fuel. It may be considered as a step towards curbing global warming and energy crisis.

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Conflicts of interest

There are no conflicts to declare.

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