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Photocatalytic Reduction of Sodium Carbonate To Formaldehyde using Graphitic Carbon Nitride – Cds – Bivo$_4$ Composite

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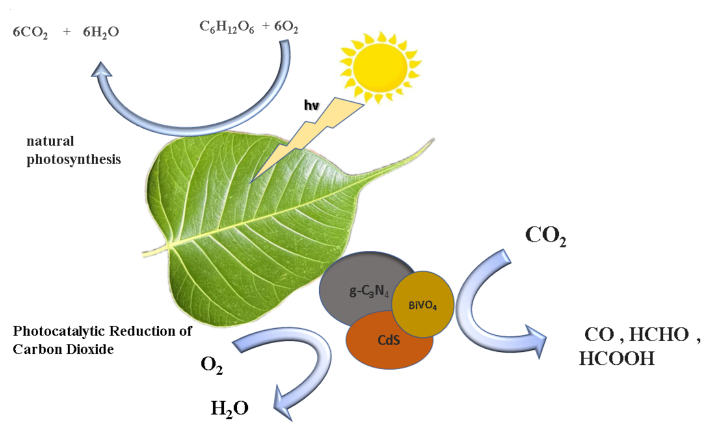
ABSTRACT

Growing energy demand challenges and environmental problems due to fossil fuel consumption have raised awareness in recent decades. Currently, the world's energy needs are largely dependent on fossil fuels such as oil, coal and natural gas. World energy consumption is constantly increasing over time with social living standards and industrialization. To solve both most pressing problems; dependence on fossil fuels and climate change, the photocatalytic reduction of carbon dioxide to produce synthetic fuels can be an attractive solution to limit environmental pollution. The conversion of CO2 into value-added chemicals by visible light driven photocatalysis has a great potential. A small amount of the composite was added to the solution of sodium carbonate and then the solution was exposed to visible light to reduce it to formaldehyde. The progress of the reaction was monitored spectrophotometrically using chromotropic acid. The effect of different operating parameters on the formation of formaldehyde was evaluated.

Key words: *Photocatalysts, Graphitic carbon nitride (g-C3N4), Environment sustainability heterojunction, Climate changes, Global warming, Sodium carbonate, Formaldehyde.*

Graphical Abstract



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Introduction

Humans is presently facing two critical problems due to the diminishing supply of fossil fuels. The first one is the scarcity of energy resources and therefore, there is an urgent need to find a pure and sustainable alternative energy source; and the second is the sharp rise in CO2 emissions in the environment, which is the main contributor to global warming. Several strategies have been tried and developed to deal with these problems such as CO2 collection and storage of CO_2, hydrogen production from water splitting and generation of carbon-based fuels from CO2 reduction, are among few of these. One of these highly promising methods is converting CO2 into useful chemicals and clean fuels, which might address both these issues simultaneously. Energy crisis and global warming has increased thrust for search of new renewable energy resources. The major component of greenhouse gases is carbon dioxide, and there is a good potential to produce synthetic fuels from its reduction. can be reduced. Scientists have made numerous efforts for photocatalytic reduction of CO2 Graphitic carbon nitride (g-C3N4) is one of most effective photocatalysis due to its heterostructures reactivity, and chemical stability, and it can absorb light. There is a necessity to develop effective photocatalyst, which can utilize light in visible range. Graphitic carbon nitride is a novel, metal-free semiconductor, and it has recently attracted significant attention of the scientists all over the globe due to its band gap in the desired range (Eg = 2.7 eV) and high stability.

The photocatalytic activity of g-C3N4 in CO2 reduction is still relatively low, but it may be enhanced by modication of g-C3N4. The g-C3N4 may be used with some other semiconductors to construct a heterojunction composite, which may prove to be an effective photocatalyst.

Reddy *et al.* (2021) reported that two-dimensional materials (2D) with heterojunction construction can be used and one can employ 0D/1D, 1D/2D, 2D/2D heterojunction to reduce CO2 into formic acid, formaldehyde, methanol, carbon monoxide etc. it was also revealed that doping different substrates into heterostructures could enhance photocatalytic activity to convert CO2 into useful products.

Ding *et al.* (2022) reported that metal-free core – shell photocatalysts consisting of graphitic carbon nitride (g-C3N4, CN) covalently linked polymers to melamine–resorcinol–formaldehyde (MRF) microsphere can be useful for this reaction. It was claimed that yield was about twenty and ten times higher as compared to its individuals' components CN and MRF, respectively. An enhanced ligand-to-ligand charge transfer was responsible for 67% of the photo-excited internal charge transfer from CN to hydroxy methylamino group in MRF, this amino group was the main catalytic site for the photocatalytic reduction of CO2 to CH3OH.

An efficient degradation of formaldehyde was reported by Liu *et al.* (2022) using flower-like Cu2"xSe/Cu2O heterojunction photocatalyst. It was reported that implantation of Cu2O lower down the work function of Cu2"xSe and boosted the collection of electrons, making heterojunction. An electron-rich area shared by Cu atoms, has active sites. The electrons in Cu2"xSe/Cu2O on illumination delocalize to attract formaldehyde molecules and converted them into semi-stable carbonates. These electrons can also react with adsorbed oxygen to produce active superoxide anion radical. They could achieve 100 and 99.5% removal percentage (CO2) and conversion rate of eliminating formaldehyde. It was suggested that Cu2"xSe/Cu2O can also be used in air purifiers.

Khodadadi-Moghaddam (2014) investigated photocatalytic reduction of carbon dioxide to formaldehyde on four different photocatalysts such as TiO2, NiO, FeS, and FeS/FeS2. They carried out this reduction in a continues flow of CO2 gas bubbled into the reactor. Sulfide ion was used as whole scavenger. It was reported that TiO2 has exhibited higher photocatalytic activity as compared to remaining three photocatalysts, The TiO2 and NiO could produce maximum formaldehyde as 720 and 380 ppm, respectively. It was interesting to note that concentration of formaldehyde was almost double when carbonate ion was added, but there was a decreasing trend in formaldehyde.

He *et al*. (2021) developed a catalyst by combining In 2O3 semiconductor and NiB amorphous alloy which exhibited very high yield of formic acid (5158.0 umol g–1h–1) on hydrogenation of carbon dioxide under sunlight irradiation. Here, In2O3 acted as a photocatalyst generating photoelectrons, which are responsible to reduce CO2 and it provided surface hydroxyl (In" OH) groups for favouring better adsorption of CO2 The NiB nanoparticles played the role of co-catalyst, as NiB amorphous alloy had good electric conductivity. It assisted transfer of photoelectrons from In2O3 ; thus photoelectron-hole recombination is reduced and quantum efficiency of this reaction was increased

Halmann *et al.* (1984) were able to reduce carbon dioxide in aqueous suspensions of titanium oxide in formic acid using using high pressure mercury lamp. formaldehyde and methanol They also observed as the reduce products. It was also reported that production rate of these products was increased in presence of titanium oxide when it was doped with RuO2. It was revealed that highest initial energy conversion efficiency of 0.04%. could be obtained. Plasmonic metallic nanoparticles can significantly enhance the catalytic efficiency of semiconductors via plasmonic photocatalysis. Pan *et al*. (20219) synthesized Ag/TiO2 hybrid photocatalyst and used it for the photochemical reduction of bicarbonate to formic acid. It was reported that TiO2 was not that efficient under solar irradiation, but format production was increased significantly on addition of silver nanoparticles. under 365 nm irradiation the photocatalytic efficiency of TiO2 was enhanced, but no effect was observed on addition of silver nanoparticles.

Qin *et al.* (2013). Descried a bifunctionalized TiO2 film two zones: Dye-sensitized zone and a catalysis zone. Then they used it for photocatalytic reduction of carbon dioxide under visible light. It was reported that charge separation could be achieved by transferring electron to catalysis zone and positive charge to anode. It was also revealed that efficient conversion of CO_2 to formic acid, formaldehyde, and methanol was there through transfer of electrons on conduction bands (CB) of titania.

Tahir and Amin (2013) investigated that role of some operational parameters, on hydrocarbon yield and selectivity pH, types of reluctant such as reduction potential. Metal-loaded and supported catalyst

Xu *et al.* (2021). prepared carbon doped In2O3 (C-In2O3) hollow tubular via calcination of MIL-68 (In) as sacrificial template. Then they prepared C-In2O3/g-C3N4 heterojunction using C-In2O3 and g-C3N4 via hydrothermal route. This hollow tubular structure, has an extended light absorption capacity and also promoted separation of photo- generated electron-hole pairs. As a result of photocatalytic reduction of CO_2 was increased . Highest CO_2 reduction to CO and CH4 was obtained as 153.42. and 110.31µmol g-1 h-1 , respectively.

Experimental section

The graphitic carbon nitrate (g-C3N4) and cadmium sulphide were purchased from the Nano Research Lab India, and ASES Works India.

Synthesis of BiVO4

Bismuth vanadate powder was synthesized by a chemical precipitation method. Bismuth nitrate pentahydrate was initially dissolved in conc. HNO3 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 titrated 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 ^{o}C overnight. It was ground and sieved followed by calcinations in air flow for 4 h at 450 ^{o}C to obtain yellow crystalline powder of bismuth vanadate.

Synthesis of ternary composite g-C3N4– CdS

The g-C3N4, CdS and BiVO4 were mixed in 1:1:1 ratio and ground in mortar with pestle.

Characterization of composite

The X-ray photoelectron spectroscopy (XPS) measurement was carried out in PHI ESCA-5000C electron spectrometer. The element composition was confirmed through an energy–dispersive X-ray spectroscopy system connected to Tecnai T-20 instrument. EDX spectrum of g-C3N4 – CdS – BiVO4 composite is given in Fig. 1.

Photocatalytic experiment

Estimation of formaldehyde - A drop of the test solution was mixed with 2 mL 12 N sulphuric acid in a test tube, then a little solid chromotropic acid or its sodium salt was added, and the tube was heated for 10 min. in a water bath at 60° C. A bright violet colour confirmed the presence of formaldehyde. The formaldehyde was estimated spectrophotometrically at λmax =nm.

Results and Discussion

These observations demonstrated that the g-C3N4 – CdS – BiVO4 is an efcient catalyst for photocatalytic reduction of CO2 into synthetic fuels (formaldehyde) for sustainable energy. Enhanced specic surface area and optical properties are usually benecial for the activity of photocatalysts. Carbon dioxide can be trapped in the form of sodium carbonate. The sodium carbonate can be reduced to formic acid and then formaldehyde. It was observed that formaldehyde can be produced in presence of g-C3N4- CdS – BiVO4 and light.

Characterization of composite

XRD Analysis

X-ray diffraction (XRD) patterns of the g-C3N4 – CdS – BiVO4 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 g-C3N4, – CdS – BiVO4 indicated that it is crystalline in nature as sharp peaks are present in XRD spectrum.

The size of these particles was determined using Debye–Scherrer equation

$D = (k\lambda/\beta \cos \theta)$

Where,

D = Crystalline size, K is the Scherer constant (K = 0.94), λ is the X-ray wavelength (1.54178Å) and β is full width at half maximum (FWHM). and θ is Braggs angle.

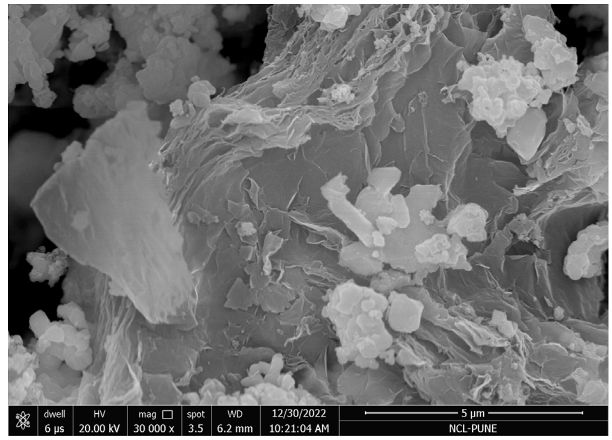
The average particle size of the sample was found to be is 1.62 nm. whivh is in the range of Quantum dots.

FESEM Analysis

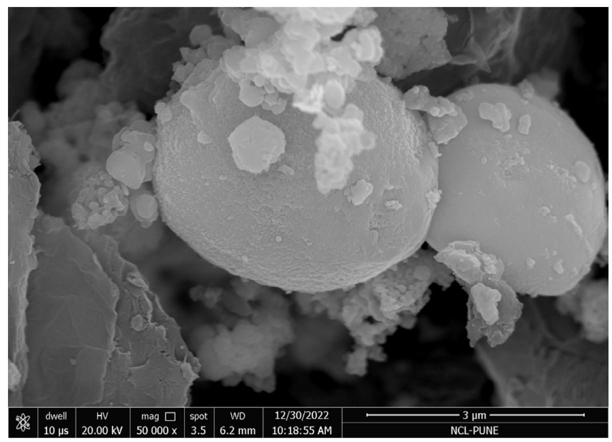
The morphology of g-C3N4, CdS,BiVO4 was investigated by FESEM (Fig. 2). It is clear from figure that it contains flakes along with Mushroom shape.

EDS Spectrum

The element composition was confirmed through an energy–dispersive X-ray Spectrum The EDS of com-



(a) Flakes of composite



(b) Mushroom shape of composite

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

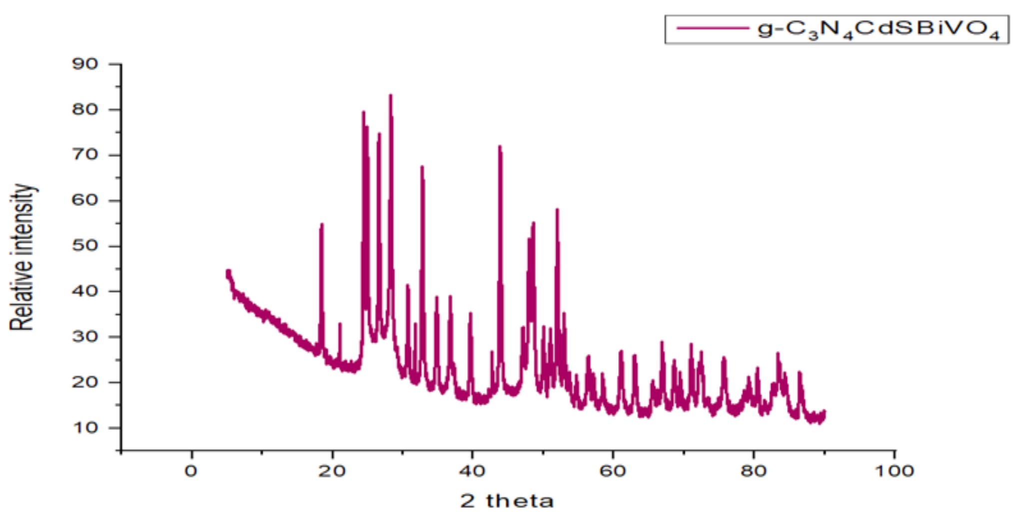


Fig. 1. XRD Pattern of composite

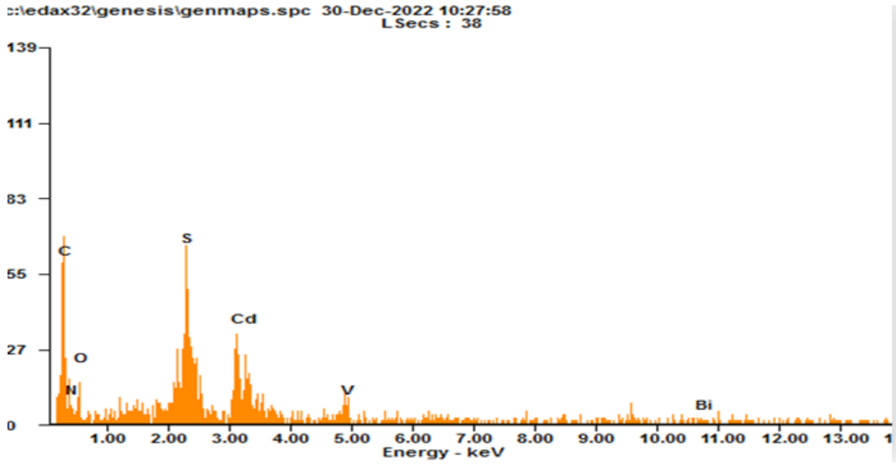


Fig. 3. EDS Spectrum

posite indicates that it contains only C, N, S, Cd, Bi, V, and O. Hence the sample is pure enough. The EDS spectrum of g-C3N4 – CdS – BiVO4 is given in Table 1.

Table. 1. EDS 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

The effect of different parameter was observed on the formation of formaldehyde

Effect of pH

Effect of pH: The effect of variation of pH was studied in the range of 8.0 – 9.0 resulted are reported in the Fig. 1.

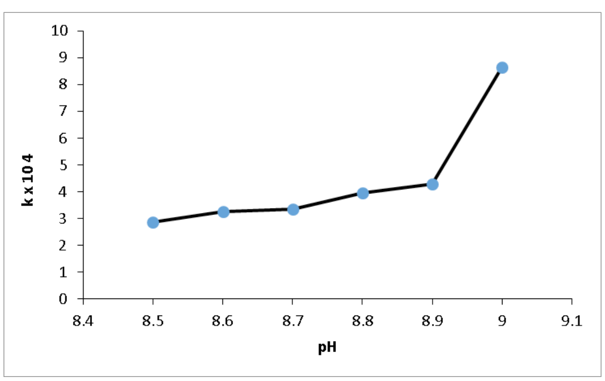


Fig. 4. Effect of pH

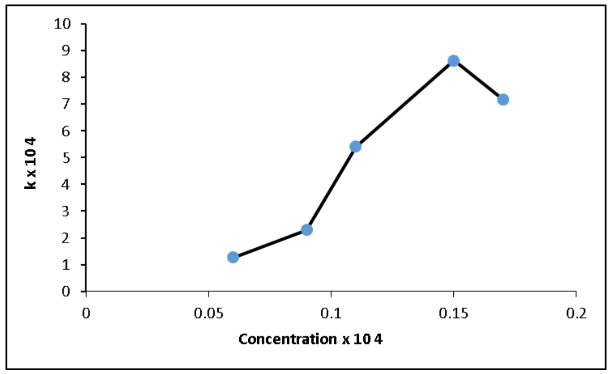


Fig. 5. Effect of Sodium carbonate concentration

Effect of Sodium carbonate concentration

The effect of concentration was observed in the range 0.61 = 1.68 × 10 -The results are reported in Table 2.

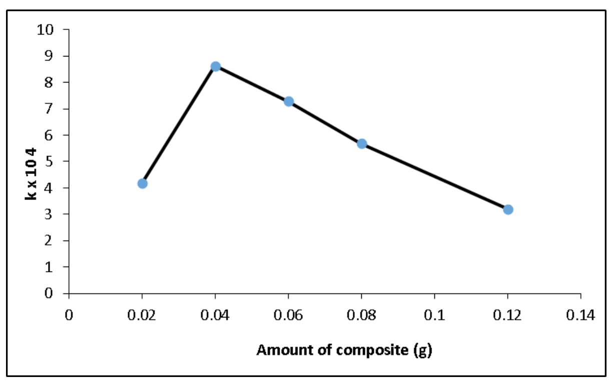


Fig. 6. Effect of amount of composite

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 – 0.12 g.

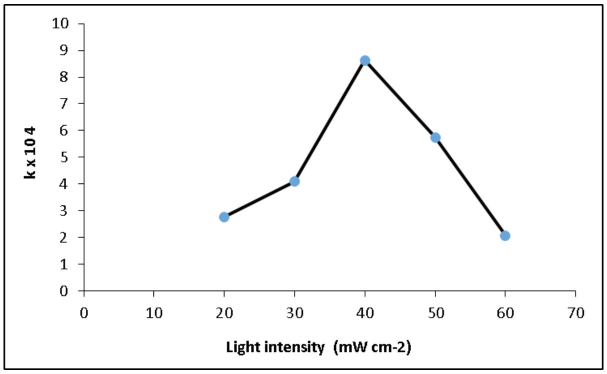


Fig. 7. Effect of light

results are reported in Table 4.

Mechanism Photocatalytic reduction of carbon dioxide

$CO_2 \xrightarrow{+e^{\cdot}} \cdot CO_2^-$ ... (1)

$\cdot CO_2^- \xrightarrow{+\cdot H}$ HO- ·C=O ... (2)

HO- ·C=O HCOOH ... (3)

$\boxed{HCOOH} \xrightarrow{+\cdot H}$ H- ·C(OH)-O ... (4)

H- ·C(OH)-OH

$\downarrow +\cdot H$ ... (5)

$\boxed{HCHO} + H_2O$

H- ·C(OH)-H $\xleftarrow{+\cdot H}$ HCHO ... (6)

$CH_3OH \xleftarrow{+\cdot H}$ H- ·C(OH)-H .... (7)

Conclusion

In summary, novel g-C3N4 CdS-BiVO4 multi hetero structured photocatalysts with high photocatalytic activity were synthesized successfully via a simple and efficient method.

g-C3N4 exhibits superior performance for photocatalytic CO2 reduction due to effective electron–hole pair separation at the composite interfaces, which in turn is based on their band positions and veried, as well as by the band positions of g-C3N4. This work has the potential to provide new insights into the development of g-C3N4 based composites as highly efcient photocatalysts for the conversion of CO_2 to fuel and a step towards curbing global warming and energy crisis.

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Conflict of Interest: None

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