On the Role of Surface Functionalities in the Photon-Assisted Reduction of Carbon Dioxide Over Graphitic Carbon Nitride ($g\text{-}C_3N_4$) Surfaces

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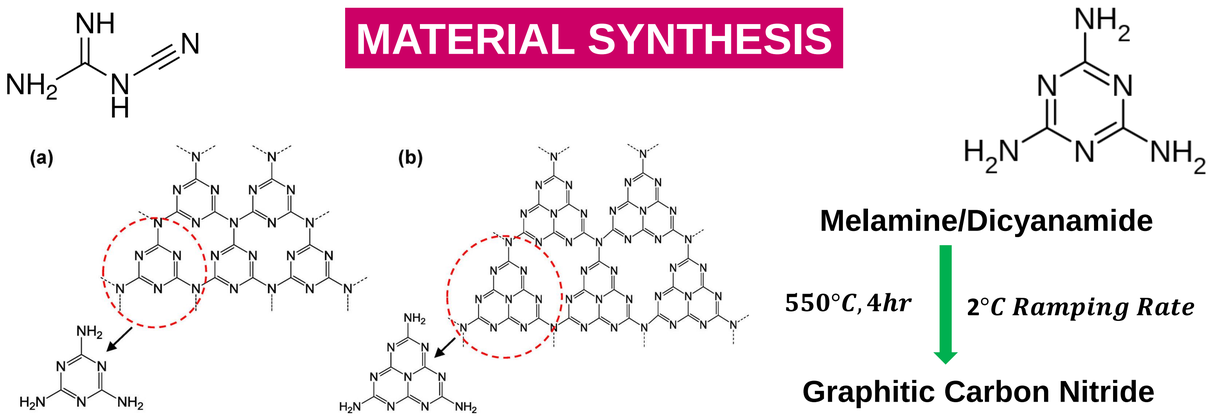
INTRODUCTION

Photon-assisted reduction of carbon dioxide is a progressing research avenue because of the ability to tackle both energy and environmental issues in a single stretch. Even though one has enough materials with appropriate band edge positions, one cannot identify a better photocatalyst with appreciable efficiency [1,2]. The way one looks forward is the induction of surface functionalities onto the photocatalyst surfaces and enhance the interaction with carbon dioxide [3]. The increased surface interaction automatically takes care of the reduction potential as well as proton-coupled electron transfer. Herein, we attempted to identify the surface functionalities responsible for the photon-assisted reduction of carbon dioxide over graphitic carbon nitride ($g\text{-}C_3N_4$) surfaces, offers a metal-free approach to the storage, activation, and subsequent conversion of carbon dioxide to fuel or fuel precursors. We have prepared the material with various precursors to obtain different surface functionalities. Based on the analyses using state-of- the-art experimental as well as characterization techniques, role of surface functionalities have been identified and an interpretation of the reaction mechanism for photon-assisted reduction of carbon dioxide on graphitic carbon nitride ($g\text{-}C_3N_4$) surfaces has been proposed.

MATERIAL SYNTHESIS



X-ray Photoelectron Spectra

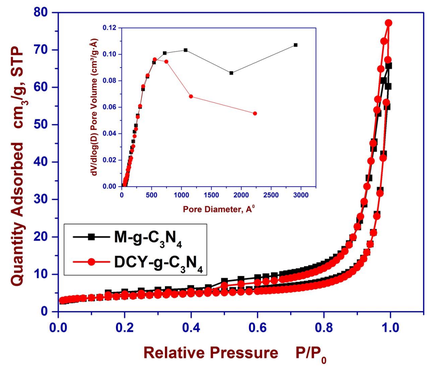
Material	Name	Pos.	FWHM	Area	% Area
		C1s			
M-g-C_3N_4	N-C=N	288.4	1.4	9240.58	66.05
	GC/ AC	284.6	2.44	1790.57	12.80
	C-NH_2	286.2	2.41	2959.38	21.15
DCY-g-C_3N_4	N-C=N	288.43	1.49	12558.23	77.40
	GC/AC	285.26	2.05	3120.93	19.24
	C-NH_2	286.65	0.92	546.10	3.37

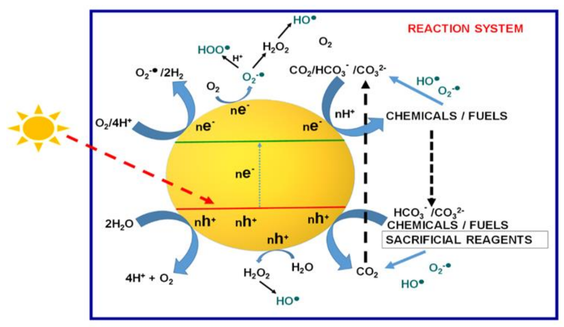
Material	Name	Pos.	FWHM	Area	% Area
		N1s			
M-g-C_3N_4	C-N=C	398.98	1.55	20947.55	72.35
	C-NH_2	400.76	2.04	6635.50	22.92
	N-$(C)_3$	397.26	2.36	1367.97	4.73
DCY-g-C_3N_4	C-N=C	399.08	1.64	21165.17	71.84
	C-NH_2	400.94	1.8	5405.10	18.35
	N-$(C)_3$	398.77	0.96	2892.40	9.82

Material	Name	Pos.	FWHM	Area	% Area
		O1s			
M-g-C_3N_4	C-OH	531.95	2.7	2546.83	100
DCY-g-C_3N_4	H-OH	532.31	1.81	1642.03	21.67
	C-OH	531.27	3.03	5935.42	78.33

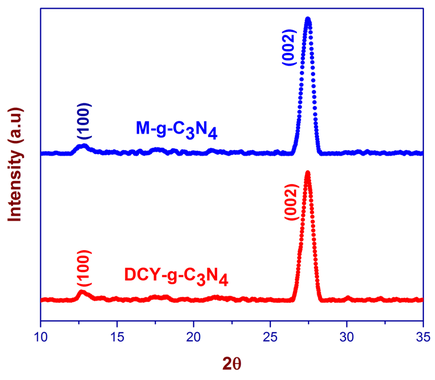
CasaXPS

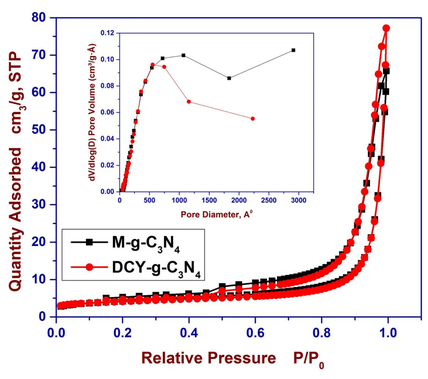
Photocatalytic CO_2 Reduction and Basic Mechanism





X-ray Diffraction Pattern and B.E.T Analysis



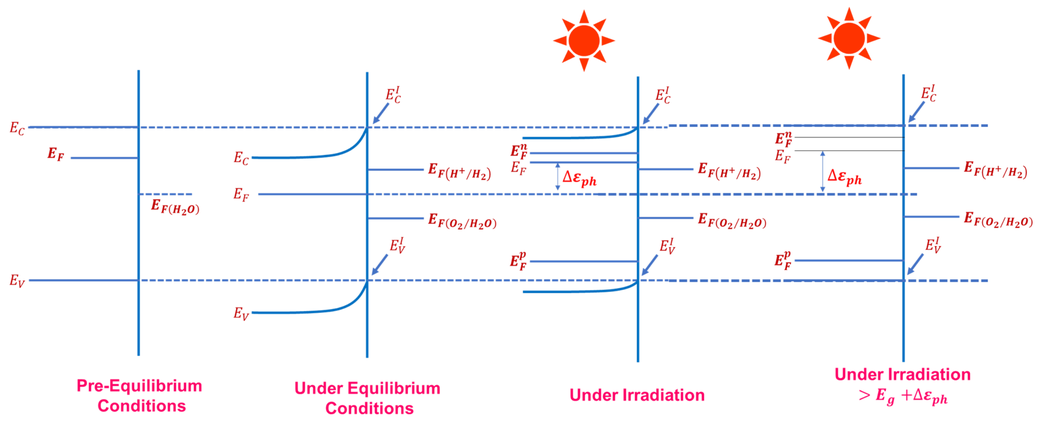


Sample	Dominant Peak Position	Peak Area	Peak Intensity	FWHM	d-spacing nm	Crystallite Size nm
M-g-C_3N_4	27.43	601.36	673	0.81	0.324	10.55
	12.88	31.3	43	0.87	0.687	9.6
DCY-g-C_3N_4	27.45	519.41	363	0.80	0.325	10.68
	12.68	29.67	44	0.72	0.698	11.6

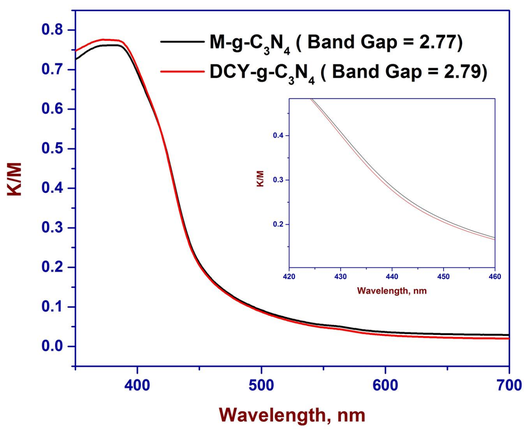
Sample	Surface Area m^2/g	Pore Size, A°	Pore Volume cm^3/g
M-g-C_3N_4	14.65	277.94	0.11
DCY-g-C_3N_4	13.64	338.89	0.12

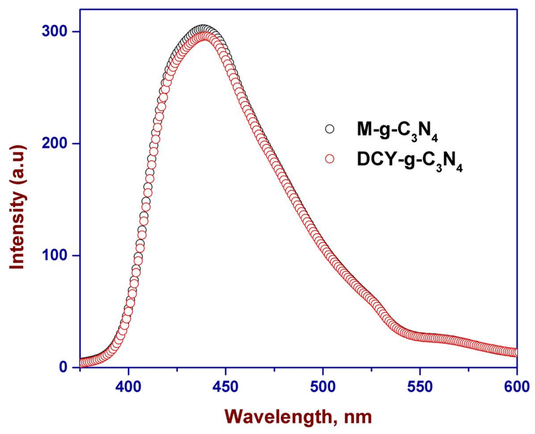
Proposed Mechanism

Why formic acid and formaldehyde formed, though graphitic carbon nitride have enough reduction potential to convert carbon dioxide into methanol/methane or any other hydrocarbons?



LIGHT ABSOPRTION PROPERTIES





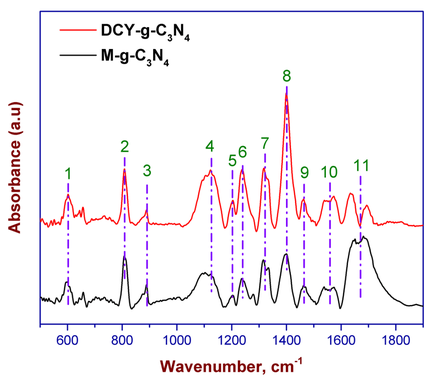
Conclusion

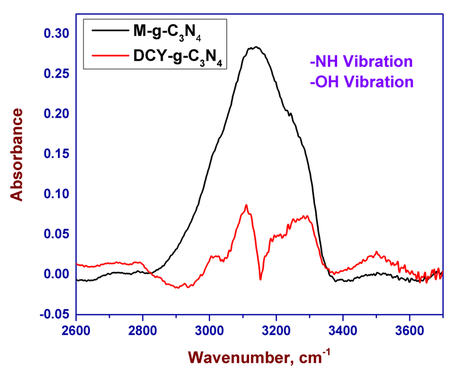
- Surface functionalities have a profound influence in driving a thermodynamically unfavourable reaction such as carbon dioxide reduction.
- The work done above point out the necessity of the study of interfaces and its characteristics under light irradiation.

Extended Work

- Extended surface functionality studies with graphitic carbon nitride having different surface functionalities.
- Real time study of semiconductor/electrolyte interface.

Fourier Transform Infrared Red Spectrum





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