DOI: 10.22607/IJACS.2017.502003

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www.ijacskros.com

Indian
Journal of Advances in
Chemical Science

Indian Journal of Advances in Chemical Science 5(2) (2017) 86-91

Modification of Metal Free Organic Semiconductor Graphitic Carbon Nitride Photocatalyst by Codoped with Diamide

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Received 03rd January 2017; Revised 31st January 2017; Accepted 03rd March 2017

ABSTRACT

Novel diamide metal free graphitic carbon nitride (CNO-g-C_3N_4) composite photocatalyst was synthesized by "in situ" chemical polymerization of urea. The resulting CNO-g-C_3N_4 composite photocatalyst was characterized by X-ray diffraction, scanning electron microscopy with energy dispersive X-ray analysis and Fourier transform infrared spectroscopy. The photocatalytic activities of the novel photocatalyst were evaluated using Rhodamine-B as a target pollutant. The CNO-g-C_3N_4 composite exhibit obviously enhanced photocatalytic performance than pure g-C_3N_4 under visible light irradiation.

Key words: *Metal free composite, Photocatalyst, Graphitic carbon nitride, Conducting polymer, Dyedegradation, Diamide.*

1. INTRODUCTION

Organic dyes are widely used in textile and food industries. On the other hand, they represent an important source of environmental contamination. Most of the dyes are toxic on aquatic creatures and have carcinogenic effects on humans [1]. Different techniques such as adsorption, oxidation, reduction, electrochemical, and membrane filtration have been applied for the removal of these pollutants from the industrial effluents [2]. Research activities in the domain of photocatalysis have acquired strong momentum in the last few years. It is now regarded as a clean and attractive, low temperature, on energy intensive approach for wastewater treatment since it achieves complete mineralization of toxic wastes.

Semiconductor photocatalysis under light irradiation has drawn much attention since the first demonstration of this concept in 1972 [3]. A number of research topics in photocatalysis have emerged and offered potential application in hydrogen production and environmental purification [4]. TiO_2 is the first and the most investigated semiconductor photocatalyst [5] its large band gap of 3.2 eV absorbing only ultraviolet (UV) light is a major drawback in its practical application [6]. To use solar energy efficient, the exploration of visible-light-induced photocatalysts has attracted a large amount of attention [7]. Many efficient visible light photocatalysts - such as modified titanium dioxide, complex metal oxides, sulfides, oxynitrides, and heterojunction structures - have been successfully designed and explored.

Recently, polymeric graphitic carbon nitride (g-C_3N_4) has induced considerable attention as a promising metal free photocatalyst working under visible light [8]. With a narrow band gap of 2.7 eV, this polymeric compound has been extensively explored as an attractive advanced semiconductor for the photocatalytic evolution of H_2 and O_2 via water splitting [9] and degradation of organic pollutants [10]. Moreover, g-C_3N_4 is composed of inexpensive "earth abundant" elements and can be synthesized by facile methods. Nevertheless, low separation efficiency of photogenerated electron-hole pairs is a main limitation of g-C_3N_4 for application [11]. To overcome this problem and improve its photocatalytic performance, numerous methods have been developed such as synthesizing mesoporus structure, nanorods, doping with metal or non-metals, coupling with other semiconductors and sensitizing by organic dyes [12].

Diamide (CNO) is one of the most intensively studied metal-free organic compounds, due to its unique electron and hole transporting properties, ease of synthesis, good chemical stability, and simple doping

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chemistry. In addition to these applications, diamide semiconductor photocatalysts have been synthesized and demonstrated higher photocatalytic activity of pollutant degradation. For example, loading some co-catalysts onto the surface of the catalyst to promote the separation efficiently of photogenerated electron-hole pairs. Another feasible strategy is to form a composite photocatalyst [13], doping or combining g-C_3N_4 with metal free semiconductor to improve its conductivity and catalytic performance.

In this study, for the first time, a CNO-g-C_3N_4 composite photocatalyst was synthesized by "in situ" chemical polymerization of diamide in the presence of g-C_3N_4 powder and the work was mainly focused on the visible light driven photodegradation of Rhodamine-B (Rh-B). The CNO-g-C_3N_4 showed significantly enhanced photocatalytic performance than pure g-C_3N_4. The improved photocatalytic activity came from the promotion of electron-hole separation caused by the synergistic effect between CNO and g-C_3N_4.

2. EXPERIMENTAL

All chemicals were analytical grade and were used without further purification. Melamine was used as the precursor in the synthesis of composite g-C_3N_4 and was purchased from Sigma-Aldrich with 99% purity, the organic solvents, and ammonium persulfate were also purchased from Sigma-Aldrich. The organic dye (Rh-B) was purchased from S.D fine chemicals India Ltd.

2.1. Synthesis of Photocatalyst

The metal-free g-C_3N_4 powder was synthesized by thermal treatment of melamine in a crucible with a cover under ambient pressure in air. After dried at 80°C for 24 h, the precursor was put in a Muffle Furnace and heated to 550°C for 3 h to complete the reaction. The product was collected and ground into a powder.

CNO-g-C_3N_4 composite photocatalyst was prepared as follows: 1.0 g g-C_3N_4, 0.034 g ammonium persufate $(NH_4)_2 S_2O_8$ (APS) and 1.5 ml 1 M HCl solution were added into 30 ml of deionized water in the reaction vessel. The mixed solution was magnetically stirred for 1 h to a uniform suspension containing g-C_3N_4 particle in an ice bath. After that, 0.1 g diamide was added to this above-cooled mixture. The resultant mixture was stirred for 2 h and allowed to react in the ice bath for 8 h. The precipitated pale yellow CNO-g-C_3N_4 composite powder was filtered and washed with ethanol and deionized water. Finally, the product was dried in a vacuum environment and the sample with CNO-g-C_3N_4 ratio 1:10 was obtained.

2.2. Characterization of Photocatalyst

The crystal structure of the samples was investigated using X-ray diffraction (XRD: Bruker D8 advanced X-ray diffractometer) with Cu Kα radiation at a scan rate of 20-80°. The morphology of the samples was examined by scanning electron microscopy (SEM: JOEL apparatus model JSM-5610LV). Chemical composition and valance band spectra of the samples were analyzed using energy dispersive X-ray microanalysis (EDAX). Infrared spectra were obtained as KBr pellets on an equinox 55 spectrometer (Bruker) in the range 4000-500 cm^{-1}. UV-visible diffuse reflectance data were collected over the spectral range 210-850 nm with Shimadzu UV-3101 PC spectrophotometer.

2.3. Photocatalytic Activity

The Photocatalytic activities of the g-C_3N_4 and CNO-g-C_3N_4 composite samples were evaluated via photocatalytic degradation of Rh-B dye in an aqueous solution under visible light irradiation.

In this experiment, 0.1 g of the photocatalyst was mixed with a 50 ml Rh-B solution (1×10^{-5} M) before irradiation, the suspensions were magnetically stirred in the dark for 30 min to achieve saturated Rh-B absorption onto the catalyst. The solution was irradiated using solar light. At irradiation time intervals of 0.5 h, the suspensions were collected and centrifuged (5000 rpm, 10 min) to remove the photocatalyst particles through a millipore filter (pore size 0.22 m). The Rh-B concentrations were monitored at 553.1 nm during the photodehydration process using a UV-visible spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis of CNO-g-C_3N_4 Composite Sample

XRD was used to determine the crystallographic structure of the organic and inorganic component of the photocatalyst. The XRD pattern of pure g-C_3N_4 is shown in Figure 1. The pure g-C_3N_4 has two distinct diffraction peaks at 27.42° and 13.1°, which can be indexed for graphitic materials as the (002) and (100). These two diffraction peaks are in good agreement with the g-C_3N_4 reported in the literature [14]. Furthermore, Figure 2 shows the XRD pattern of the as prepared CNO-g-C_3N_4 composite. It shows the strong and sharp peaks at 6.2°, 11.1°, 12.5°, 27.42° suggest that the prepared materials are crystalline.

3.2. Fourier Transform Infrared (FT-IR) Analysis

The molecular structure of the resulting CNO-g-C_3N_4 composite photocatalyst is characterized by FT-IR spectroscopy. Figure 3 shows the FT-IR spectrum of pure g-C_3N_4 and Figure 4 shows the FT-IR spectrum of CNO-g-C_3N_4 composite. The main characteristic peaks of pure g-C_3N_4 can be assigned as follows: The bands at 1242, 1327, 1411 and 1566 cm^{-1}, which can be assigned to the typical stretching modes of C-N heterocycles [14]. Moreover, the characteristic breathing modes of triazine units at 810 and 887 cm^{-1}.

The band at 3170 cm^{-1} can be attributed to hydrogen bonded N-H bond between amine and imine sites. The band at 1905 cm^{-1} is due to strong C=N stretching vibration. For CNO-g-C_3N_4 composite photocatalyst also similar to those of the bands of pure g-C_3N_4, but an additional band appears at 1851 cm^{-1} is due to strong C=O stretching vibration mode of keto group present in diamide.

3.3. Surface Characteristics of the Sample

The morphology of pure g-C_3N_4 and CNO-g-C_3N_4 composite samples were characterized by SEM. Figure 5a-c shows the SEM images of the pure g-C_3N_4 and Figure 6a-c shows the SEM images of CNO-g-C_3N_4 composite samples. Both the samples display aggregated morphologies. The pure g-C_3N_4 sample appears to have aggregated particles which contain many smaller crystals. After introducing the CNO, the CNO particles can be found on the surface of g-C_3N_4 particles, forming an intimate interface between CNO and g-C_3N_4 in composite photocatalyst.

3.4. Elemental Analysis of the Sample

Figure 7 shows the EDAX.patterns of the g-C_3N_4 and Figure 8 shows the EDAX patterns of CNO-g-C_3N_4 composite sample. EDAX indicated C, N as the major elements in pure g-C_3N_4 photocatalyst. Figure 8 confirms the presence of dopant C, N, and O which are indicated by the strong peaks. Table 1 indicated by the atomic and mass percentage of the pure g-C_3N_4 and theCNO-g-C_3N_4 composite samples.

3.5. Photocatalytic Activity of the Photocatalys

The photocatalytic activity of CNO-g-C_3N_4 composite sample was investigated by choosing the photodehydration of Rh-Bdye in aqueous solution under visible light irradiation. Samples were

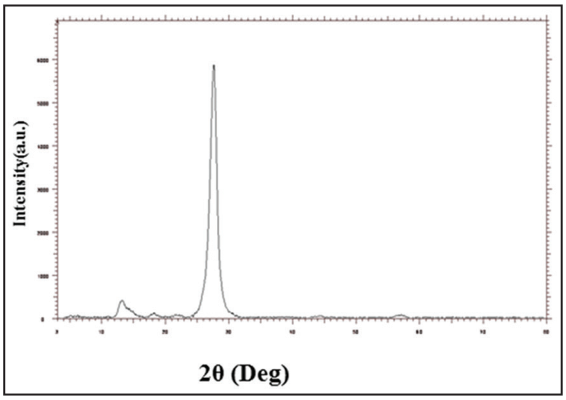

Figure 1: X-ray diffraction pattern of pure graphitic carbon nitride.

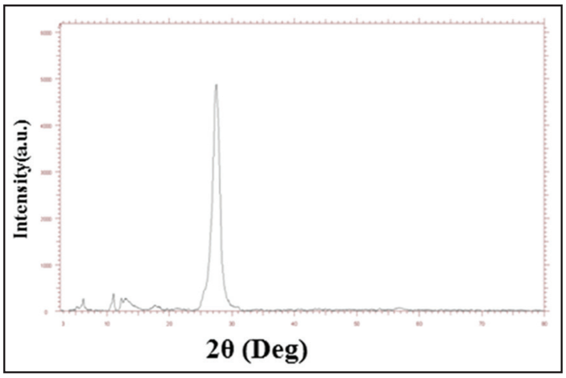

Figure 2: X-ray diffraction pattern of CNO-graphitic carbon nitride composite photocatalyst.

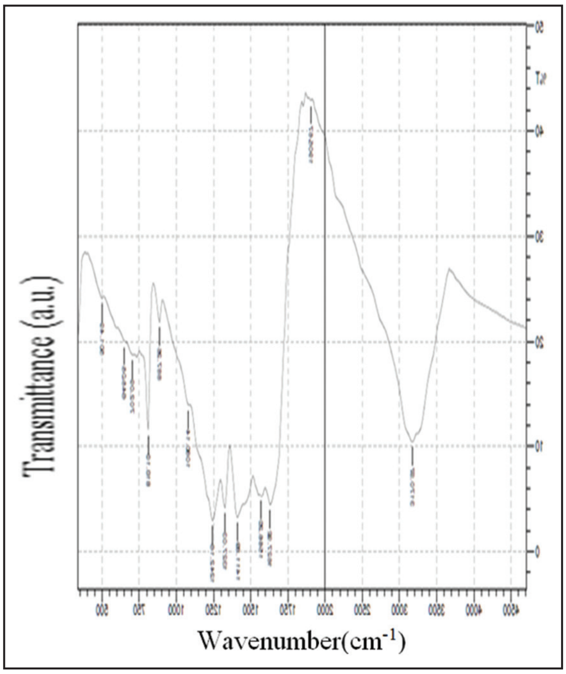

Figure 3: Fourier transform infrared spectrum of pure graphitic carbon nitride.

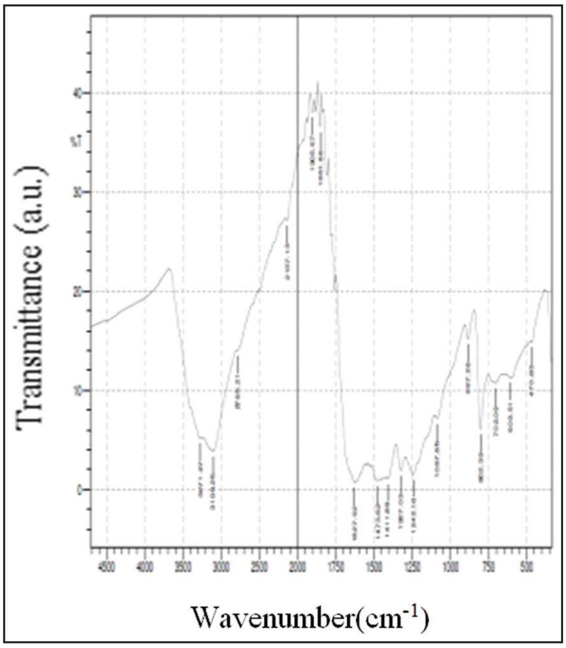

Figure 4: Fourier transform infrared spectrrum of CNO-graphitic carbon nitride composite.

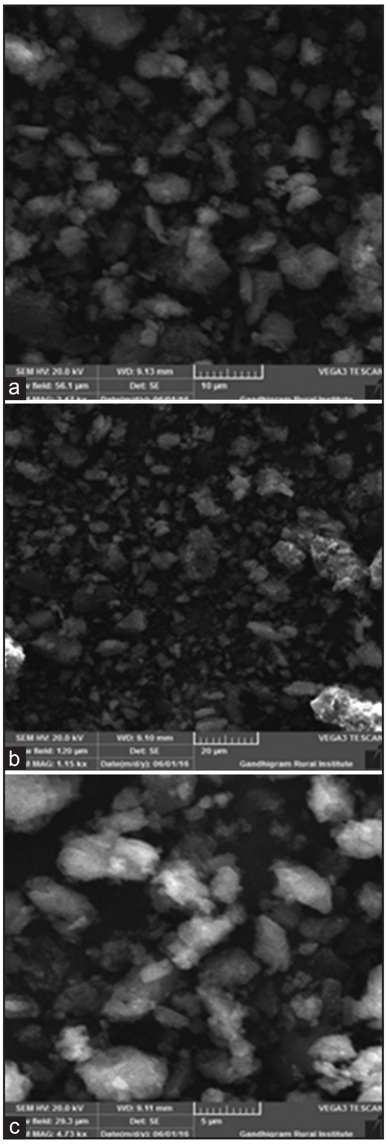

Figure 5: (a-c) Scanning electron microscopy images of pure graphitic carbon nitride.

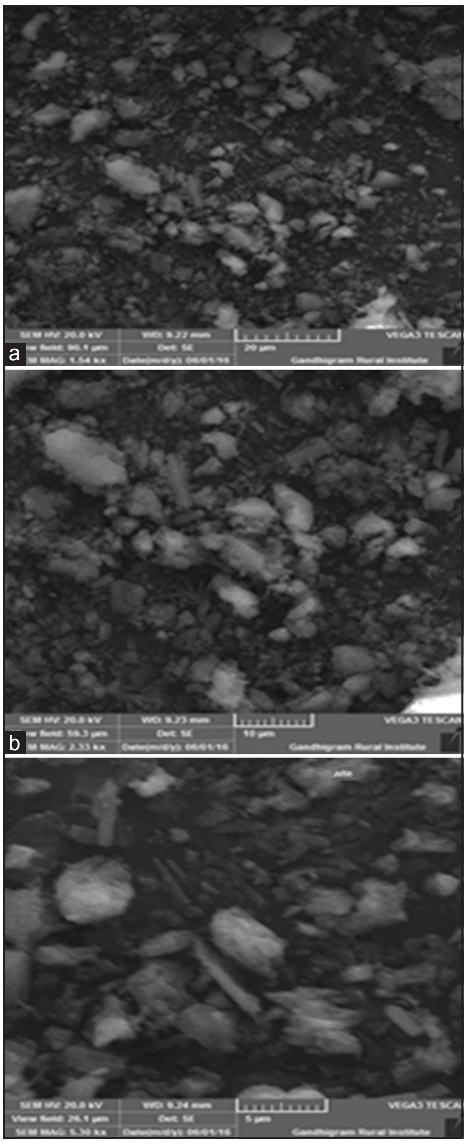

Figure 6: (a-c) Scanning electron microscopy images of CNO-graphitic carbon nitride composite.

withdrawn periodically centrifuged and analyzed for the degradation of Rh-B using a UV-visible spectrometer. Rh-B has the maximum absorbance at 553.1 nm was employed to monitor as shown in Figures 9 and 10 shows the photocatalytic activity of the CNO-g-C_3N_4 composite sample. Table 2 shows the degradation efficiency of Rh-B during 120 min illumination under visible light using pure g-C_3N_4 and CNO-g-C_3N_4 composite catalyst.

Table 1: Atomic and mass percentage of pure g-C_3N_4 and CNO-g-C_3N_4 composite.

Sample	Elements	Mass%	Atom%
g-C_3N_4	N	66.54	63.04
	C	33.46	36.95
	Total	100.00	100.00
CNO-g-C_3N_4	N	58.15	54.53
	C	40.73	44.55
	O	1.12	0.92
	Total	100.00	100.00

g-C_3N_4: Graphitic carbon nitride

4. CONCLUSION

Novel CNO-g-C_3N composite photocatalyst was successfully prepared via "*in situ*" chemical polymerization of urea. The surface morphology and elemental analysis of the composite have been investigated and discussed. The FT-IR results confirm that interaction has been formed between CNO and g-C_3N_4 in the composite photocatalyst and the CNO-g-C_3N_4 composite exhibit stronger absorption in the visible region. The composite sample shows significantly enhanced photocatalytic activity in

Table 2: Degradation efficiency of Rhodamine-B during 120 min illumination under visible light using pure g-C_3N_4 and CNO-g-C_3N_4.

Photocatalyst	Wavelength (nm)	I_0	0.5 h	1 h	1.5 h	2 h	Degradation efficiency %
Pure g-C_3N_4	553.1	1.007	0.936	0.756	0.701	0.592	40.5
CNO-g-C_3N_4	553.1	1.172	0.721	0.500	0.355	0.22	81.2

g-C_3N_4: Graphitic carbon nitride

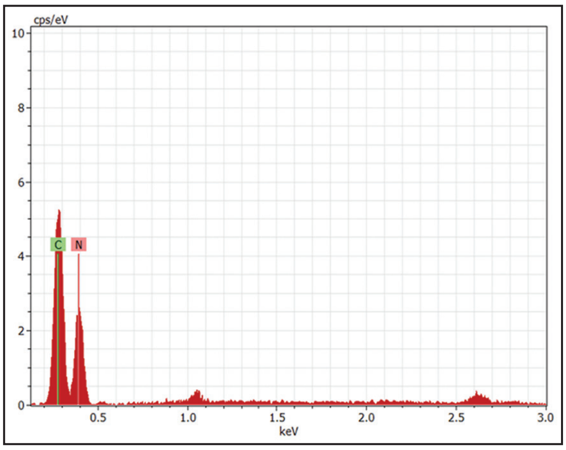

Figure 7: Energy dispersive X-ray spectrum of pure graphitic carbon nitride.

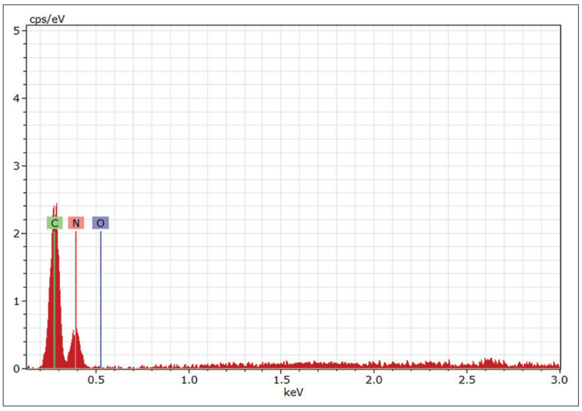

Figure 8: Energy dispersive X-ray spectrum of CNO-graphitic carbon nitride composite.

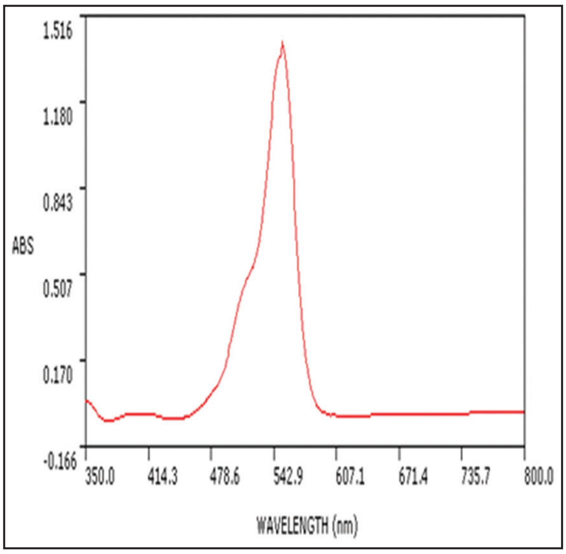

Figure 9: Ultraviolet-visible spectrum of the dye Rhodamine-B.

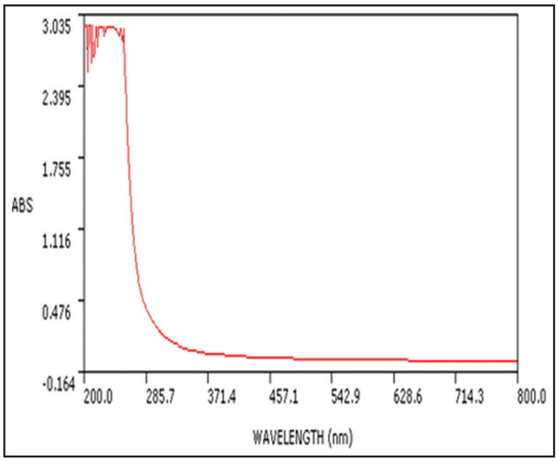

Figure 10: Ultraviolet-visible degradation spectrum of Rhodamine-B dye using CNO-graphitic carbon nitride.

the degradation of Rh-B dye than pure. The higher activity of metal-free organic composite photocatalyst has promising potential application.

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***Bibliographical Sketch**

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