Electronic Supplementary Information

Microwave assisted *in situ* decoration of g-C_3N_4 surface with $CdCO_3$ nanoparticles for visible light driven photocatalysis

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Section S1. General information

All chemicals, Melamine (Finar Chem. Ltd, 99%), Cadmium chloride hydrated ($CdCl_2.2H_2O$) AR (s.d. fine chem. Ltd. 99.5%), Urea (Qualigens, 99%), Ethylene glycol (Merck, 99%) and Indigo carmine-Acid Blue 74 (Aldrich, dye content ca. 85%), were of analytical grade and used as received without any further purification. Millipore water (conductivity < 0.15 mS cm^{-1}) was used for all experiments.

Section S2. Characterisation

Powder X-ray diffraction analysis of the samples was performed for the structural characterisation using Rigaku: Miniflex-II-DD34863 X-ray diffractometer with Cu Kα radiation (λ = 0.15418 nm) operated at 30 kV and 15 mA at a scan rate of 10° min^{-1}. The surface area was determined by Brunauer–Emmet–Teller (BET) method using Micromeritics ASAP 2020 V3.04 H surface area analyser by nitrogen adsorption at 77 K. The TEM images were taken using a FEI Tecnai T-20 electron microscope operating at 300 kV. Energy dispersive X-ray spectroscopy analysis was carried out using FEI Quanta 200 ESEM. UV-visible diffuse reflectance spectra (UV-vis DRS) of all samples were recorded using a Jasco (model V-670) spectrophotometer equipped with an integrating sphere accessory. Barium sulfate was used as reference for the reflectance spectra.

Section S3. Experiments description

Photodegradation Experiments

Photocatalytic activity of the samples was studied for the degradation of IC (50 mgL^{-1}) as per our previous reports.[1-3] In brief, a fluorescent lamp was used as source of radiation which contains visible light along with ~3% UV radiation.[4] A homemade photo irradiator, which is a rectangular galvanised iron sheet box fitted with fluorescent lamps (12 lamps of 100 watts each, Oreva) vertically and equidistantly on the base of the chamber was used for photocatalytic experiments. The average light flux measured by a digital lutron lux metre (model LX-101) was found to be 60,000–65,000 lux. The photocatalytic experiment was performed in a beaker containing 125 ml of 50 mgL^{-1} IC and 0.35 g of catalyst under ambient conditions. Before irradiation, the samples were magnetically stirred in the dark for 30 minutes to ensure uniform dispersion and adsorption-desorption equilibrium between the dye molecules and the catalyst surface. After irradiation, 5 mL sample aliquot was extracted for analysis at an interval of 5 min, centrifuged and quantitative determination was carried out by measuring its absorbance at λ_{max}=610 nm using a UV-vis spectrophotometer (Shimadzu, UV-1800). Concentration of IC solution remained unchanged when it was irradiated without catalyst. Stability of the catalyst was tested by reusing the catalyst for repeated cycles of experiment after a photocatalytic reaction. After each cycle of experiment, the used catalyst was removed from the reaction mixture by centrifugation, washed with millipore water and acetone followed by drying in vacuum oven at 80°C for 2 h. The degradation efficiency of IC was calculated by using the following equation.

$$\% \text{ degradation} = \frac{C_o - C_t}{C_t} x\, 100 \qquad (1)$$

Where C_0 and C_t are the concentration of IC at time t and 0 respectively. The reaction rate (k) was calculated from the slope of straight line obtained by plotting ln C/C_0 versus illumination time, (t) as

$$\ln\frac{C}{C_0} = -kt \quad (2)$$

Where t is the irradiation time, k is the first-order rate constant of the reaction, C and C_0 are concentration of dye at time t and 0 respectively.

Bacterial culture and antibacterial study

Gram-negative *E. coli (E. coli*) (ATCC 25922) was selected as the model target microorganism for antibacterial tests. Before, experiments all the glassware were sterilised by autoclave at 120°C for 30 min. For photocatalytic bactericidal experiments, *E. coli* was transferred to 30 mL of liquid Luria Bertani (LB) culture medium from solid LB agar plate and grown at 28°C for 12h. Then the bacteria were diluted with broth to 10^5 cfu/ml and concentration of bacteria was determined by measuring optical density at 600 nm. Certain amount of catalyst was suspended in 30 mL of *E. coli* culture medium solution, having concentration

n of 10^5 cfu /mL. Prior to exposure of light, the culture mixture was magnetically stirred in the dark for 30 min. The source of illumination used was 200watt tungsten lamp. The light source was located 22 cm away from the sample. To quantify the antimicrobial results, about 1 ml of the suspended bacteria solution was withdrawn after the photo irradiation to ensure the growing bacterial colonies were legible. Then 0.1 mL of the treated solution was spread on solid LB medium. The colonies were continued to incubate at constant temperature of 28°C for 24 h and then counted to determine the bactericidal efficiency. For better comparison, control experiments were carried out simultaneously without catalyst and without light illumination. The percentage of growth inhibition was determined by comparing the survival colony counts with corresponding colony counts of control sample.

ITO electrode preparation

Electrochemical impedance spectroscopy of the prepared catalyst was studied by coating it on to the conducting ITO (indium tin oxide) glass electrode. For this 100 mg catalyst was mixed with 50 mg ethyl cellulose, 0.32 mL terpineol, 20 µL of acetic acid and ethanol solvent to get uniform paste and then drop coated onto ITO glass electrode.[5] Solvents were allowed to evaporate from the electrode by drying them at 80°C in an oven**.**

Mass spectrometry

The identification of degradation products was performed by using a Waters Micromass Q-TOF mass spectrometer, Waters Alliance 2795 elctrospray ionisation mass spectrometry (ESI-MS). Ion Trap mass spectrometer was operating in negative ion mode with the capillary and cone voltage of 3 kV and 30 V, respectively, and a desolvation temperature of 300°C. To each sample (20 µl), 1 ml solution of methanol/deionised water (7: 3 v/v) and 0.1 ml aqueous solution of ammonia (0.1% v/v) were added. This diluted solution was then directly infused into the ESI source at a flow rate of 0.3 ml min^{-1} via a micro syringe pump. The mass analyser was set to operate at a scan range of 50–450 *m/z*. The product ion MS analysis was accomplished with the high-resolution orthogonal TOF analyser.

Section S4. Adsorption Study

Adsorption of IC on the catalyst surface is further confirmed by recording the FTIR spectra of the catalyst after keeping in contact with the dye solution for 90 min. FTIR spectrum of g-C_3N_4/$CdCO_3$-90 catalyst after adsorption of the dye under dark conditions and after the complete degradation reaction along with fresh g-C_3N_4/$CdCO_3$-90 is shown in **Figure S5.** The spectrum of the composite after the dark adsorption has shown several new peaks which are due to the adsorption of IC onto the catalyst surface. A sharp asymmetric stretching vibration at around ~1300-1250 cm^{-1} is due to the perpendicular adsorption of two sulfonyl groups of IC onto carbonate part of catalyst.[44] This is in good agreement with the already reported data on IC adsorption through sulfonyl bonding mode.[45] A very broad trough from 1670-1512 cm^{-1} is observed after dark adsorption, which is attributed to aromatic stretching vibration of IC.[45] These observations confirm that adsorption of IC on catalyst takes place during the initial equilibration period. After irradiation for 40 min, aromatic stretching bands due to dye adsorption have disappeared suggesting the photocatalytic degradation of dye. The FTIR spectrum of g-C_3N_4/$CdCO_3$-90 after photocatalytic reaction is almost similar to that of fresh catalyst suggesting that the photodegradation of the dye takes place on the catalyst and it is not just the adsorption of the dye occurs on the catalyst surface.

Section S5. Intermediates study

At first, starting from anionic form of IC, the formation of **1b** (*m/z* 226) from **1a** is described as arising from photochemical and photocatalytic degradation of IC [50] and formation mechanism is given in **scheme S2.** The carboxylic acid **1c** (*m/z* 244) was anticipated to be formed by the nucleophilic attack of a water molecule on the carbon of the -HNCO-moiety of **1b** followed by the lactam ring opening. Formation of **1d** (*m/z* 216) and **1e** (*m/z* 200) is proposed to be formed by the subsequent reduction of carboxyl intermediate **1c**. Finally, the anion **1f** (*m/z* 171) was expected to be formed via the release of CO from **1e**. It is believed that the formed anion **1f** further transformed to produce acetamide of m/z 60, which gets hydrolysed to form acetic acid. Previous reports suggest that acetic acid require longer time for mineralization before producing CO_2 and water molecules.[45] The ESI-MS analysis after 30 min interval shows intense high abundant m/z 60 peak of acetic acid**,** which decreases significantly (after 180min of irradiation) as reaction proceeds (**Figure S8)**. Thus, the degradation pathway of IC follows by the formation of carboxylic acids of lower molecular weight and their decarboxylation evolving carbon dioxide and water molecules. These studies reveal that almost complete mineralization of IC dye occurs using g-C_3N_4/$CdCO_3$-90 catalyst under visible light irradiation. The plausible pathway for the degradation of IC in aqueous solution over g-C_3N_4/$CdCO_3$ composite is illustrated in **Scheme S3**.

Figure S1. Digital photograph of SINEO UWave-1000 microwave synthesizer used in the study.

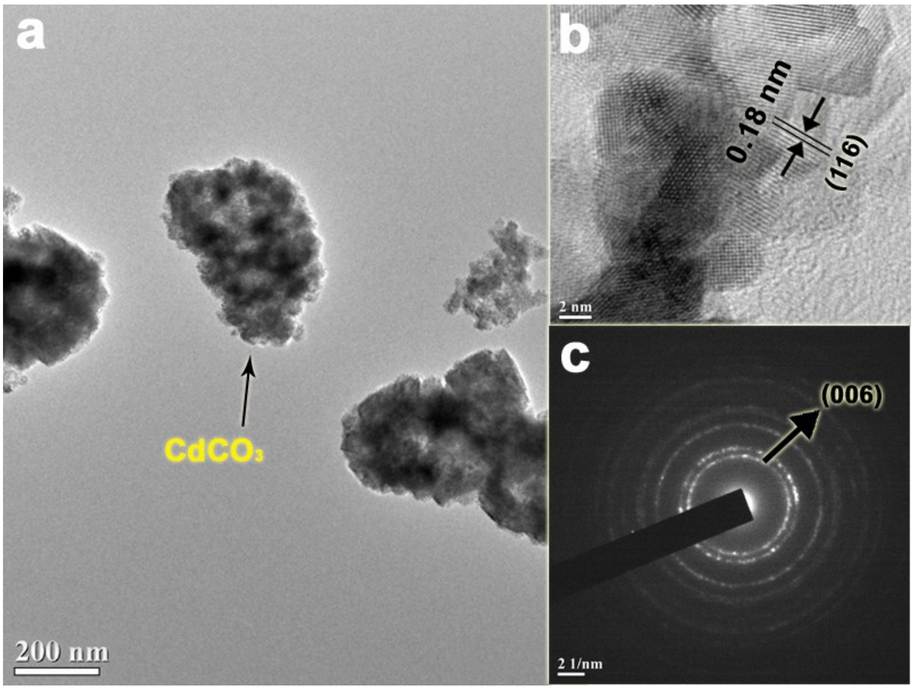


Figure S2. TEM image, HRTEM and SAED pattern of $CdCO_3$

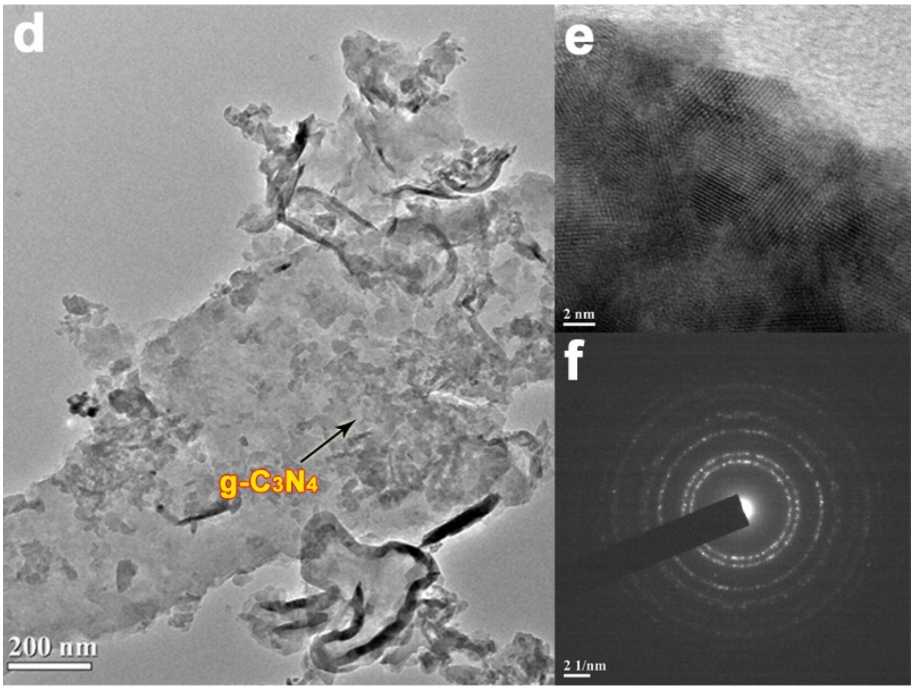


Figure S3. TEM image, HRTEM and SAED pattern of g-C_3N_4

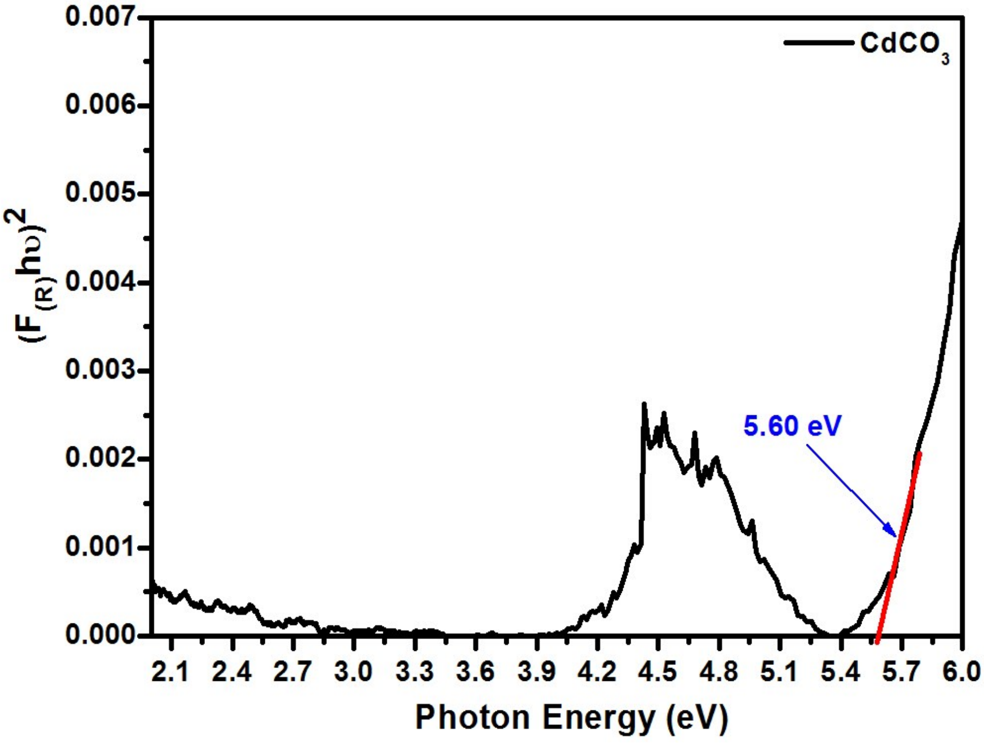


Figure S4. Kubelka–Munk plot for band gap calculation of $CdCO_3$

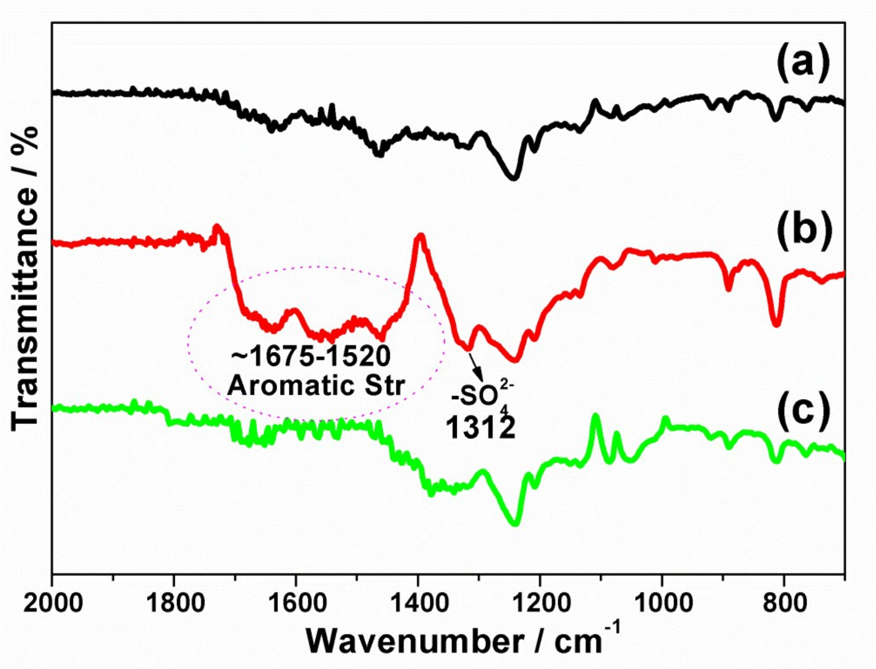


Figure S5. FT-IR spectra of (a) g-C_3N_4/$CdCO_3$-90 fresh (b) g-C_3N_4/$CdCO_3$-90 after keeping in IC dye solution (50 mg/L) and (c) g-C_3N_4/$CdCO_3$-90 after photodegradation reaction.

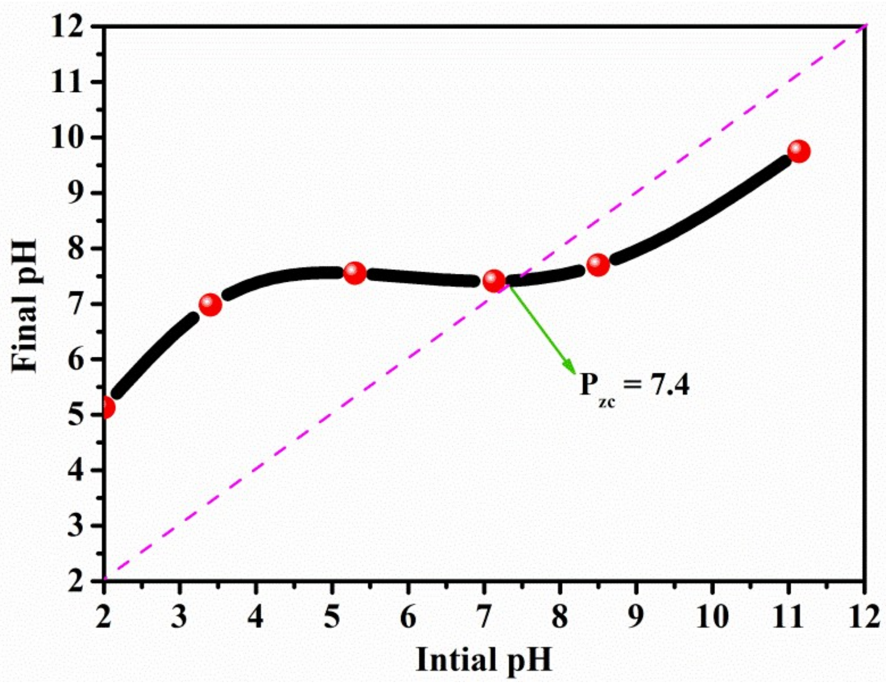


Figure S6. Point zero charge (PZC) of g-C_3N_4/$CdCO_3$-90 composite.

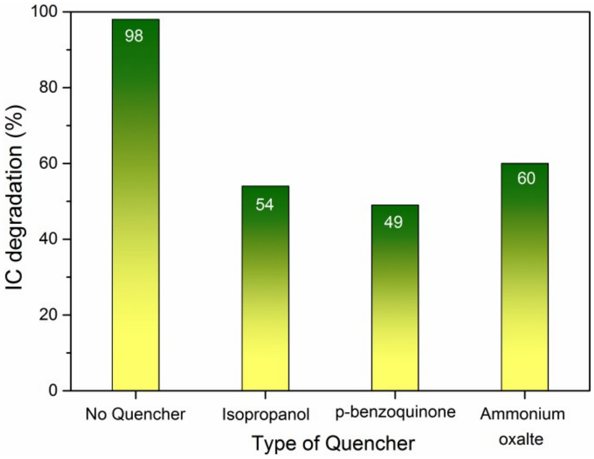


Figure S7. Effect of quenchers on the photodegradation of IC using g-C_3N_4/$CdCO_3$ nano-composite photocatalyst.

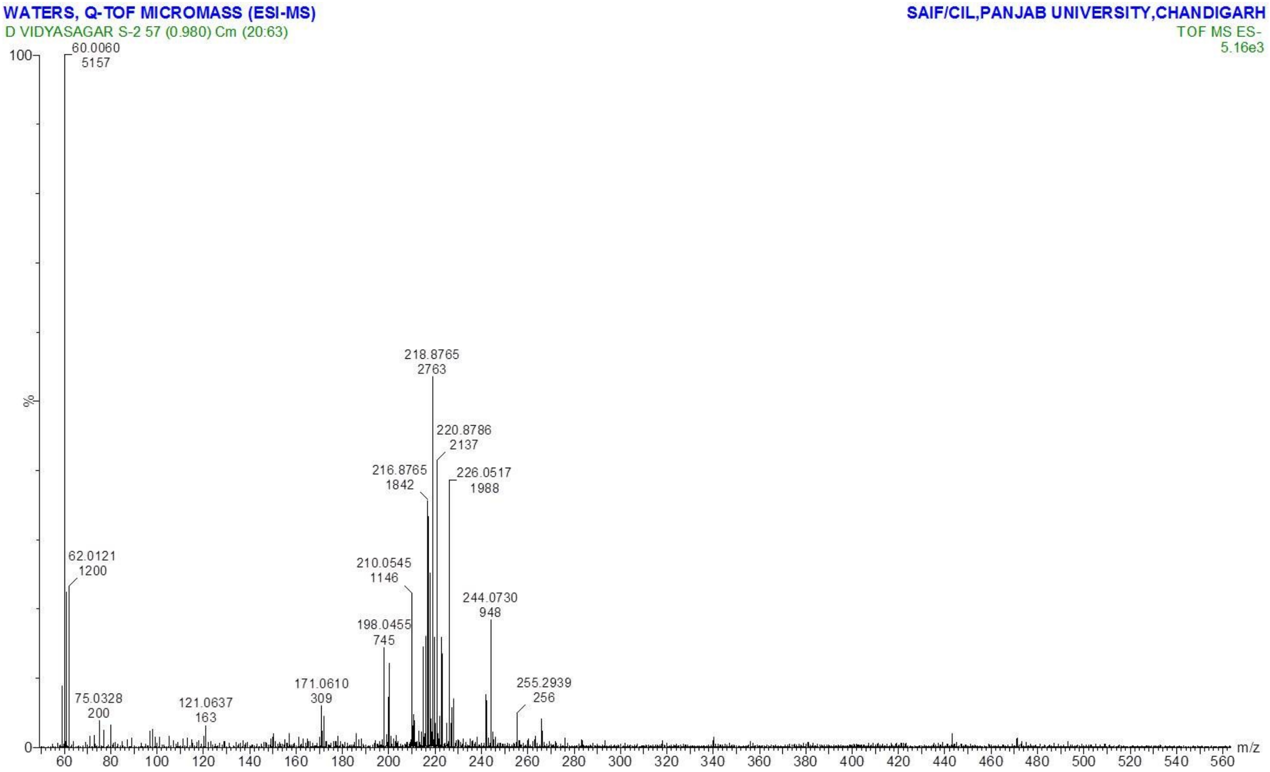


Figure S8. ESI (-) Mass spectra of IC dye solution after 30 min of irradiation.

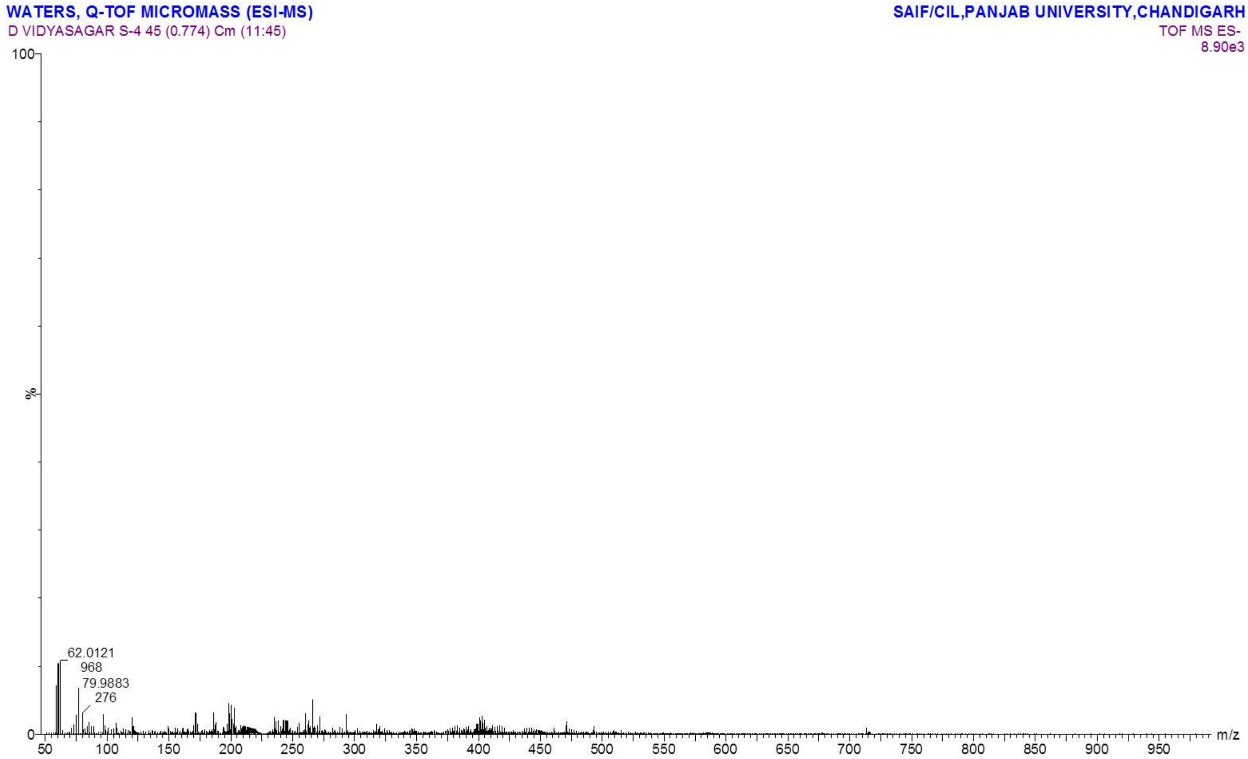


Figure S9. ESI (-) Mass spectra of IC dye solution after 180 min of irradiation.

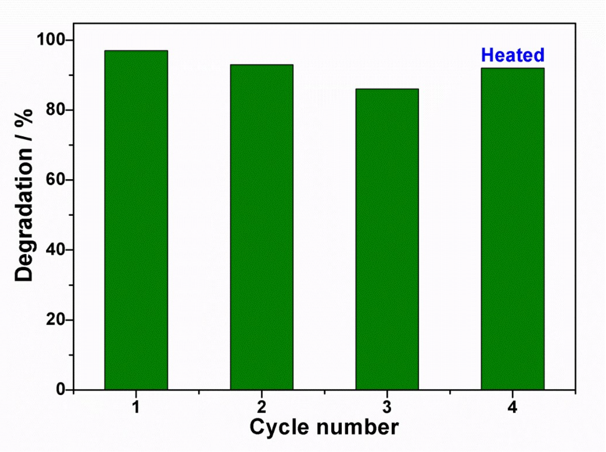


Figure S10. Recyclability study of g-C_3N_4/$CdCO_3$-90 composite for four repeated cycles (IC dye; 50 mg/L).

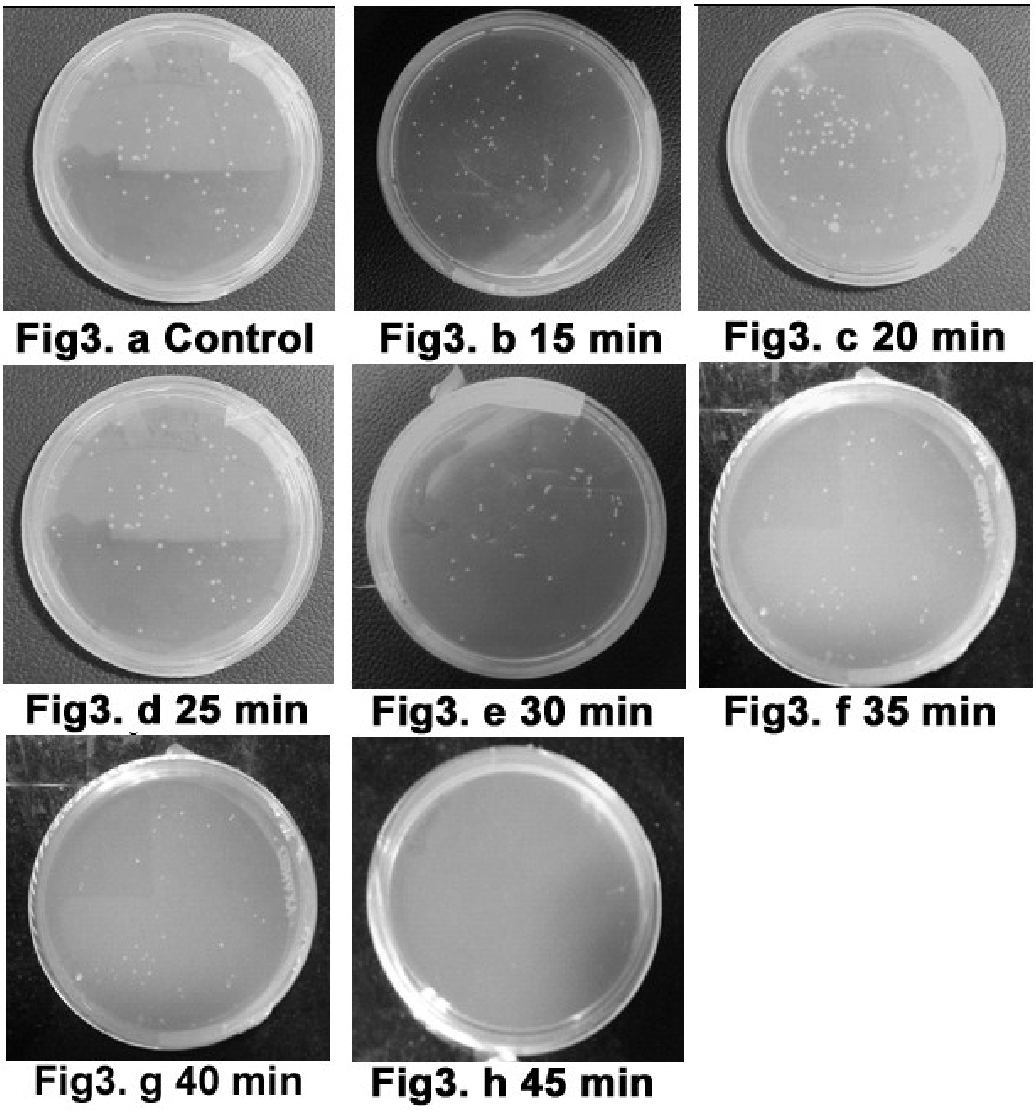


Fig3. a Control

Fig3. b 15 min

Fig3. c 20 min

Fig3. d 25 min

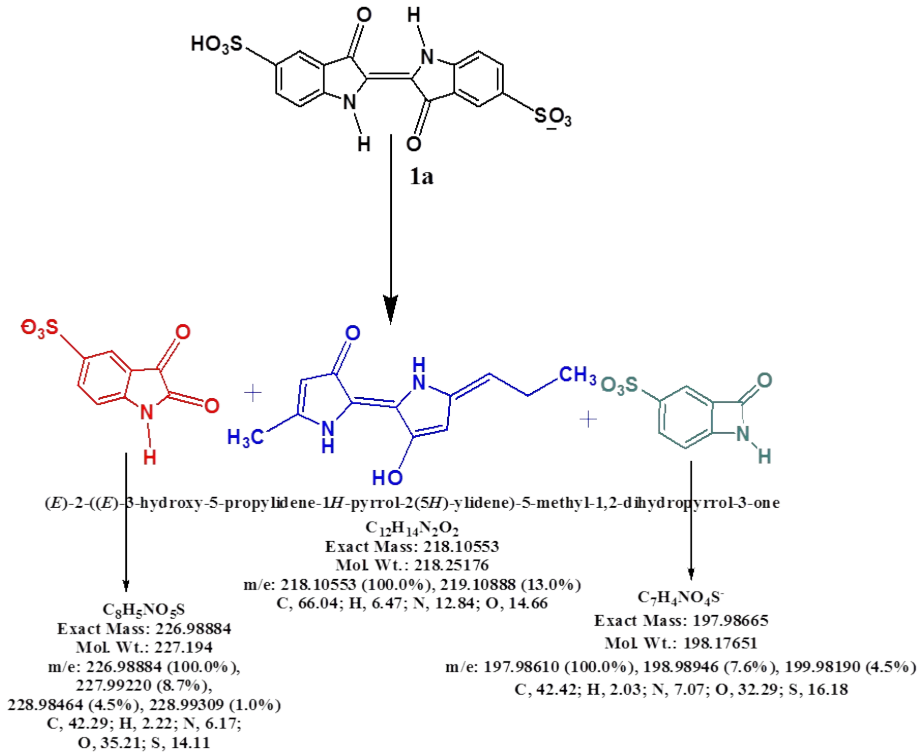
Fig3. e 30 min

Fig3. f 35 min

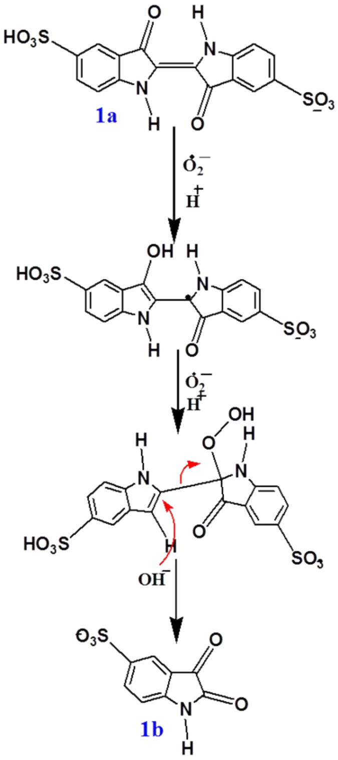
Fig3. g 40 min

Fig3. h 45 min

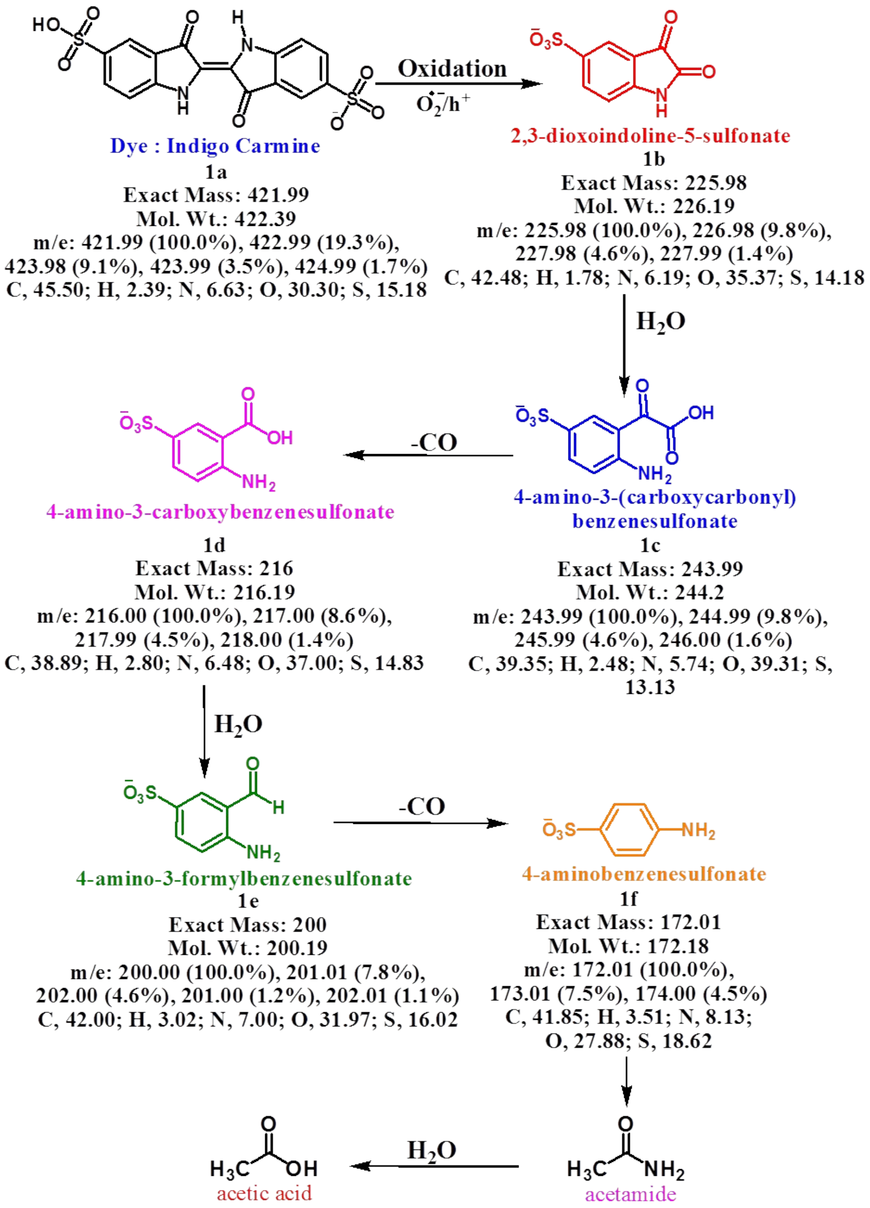
Figure S11. (a) Growth of *E.coli* in dark as a control and samples were drawn within fixed time interval (Fig 3b-3h) and incubated with g-C_3N_4/$CdCO_3$-90 irradiated under visible light. The images are taken following incubation on solid LB medium for 24 h.



Scheme S1: Fragmentations observed upon mass selection and dissociation of parent IC anion.



Scheme S2: Plausible photochemical degradation of IC and reaction mechanism for the formation of **1b** from parent molecule.[6]



Scheme S3: Plausible pathway for the degradation of IC in aqueous solution over g-CN/$CdCO_3$ composite.

References

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