Supplementary Information

Enhanced Synergistic Photocatalysis: A Thorough Investigation of $Bi_2Sn_2O_7/C_3N_5$ Heterojunctions

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1. Different control experiments for the *o-DCB* degradation.

a. Self-degradation of *o-DCB* under visible light & adsorption of *o-DCB* over photocatalysts in dark. (Photo-catalytic activity)

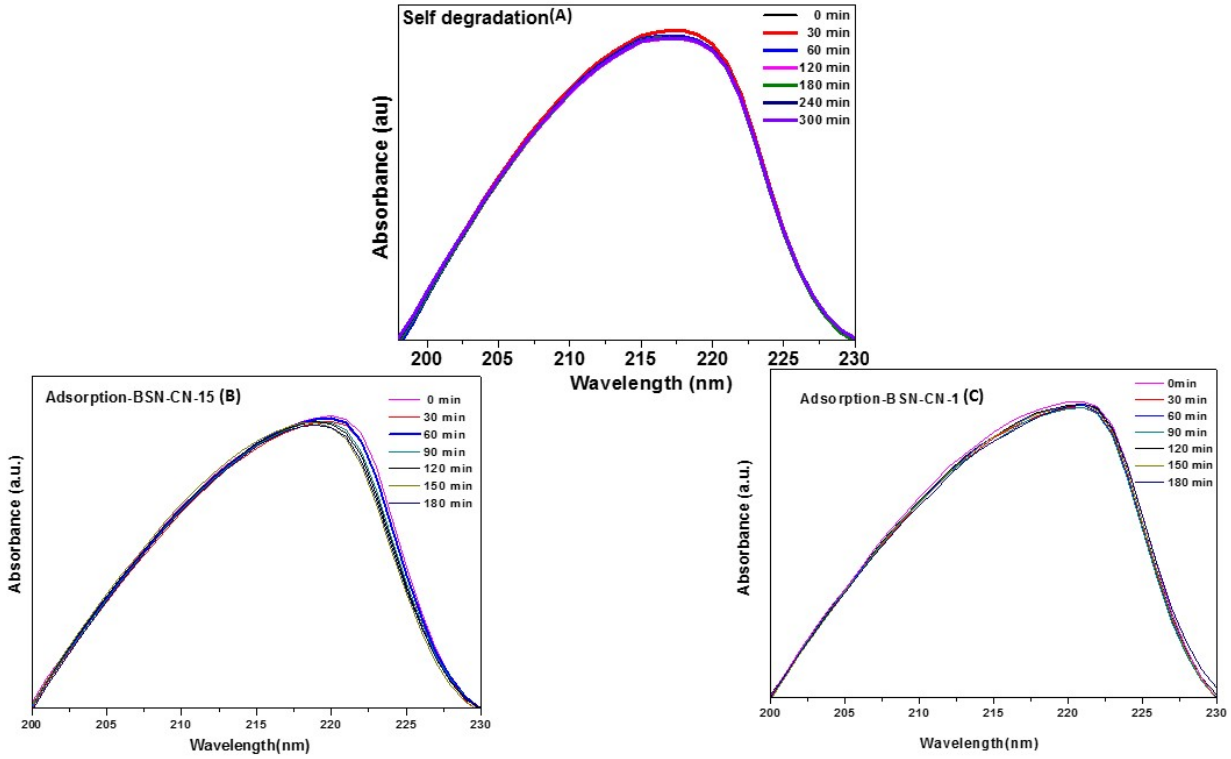


Fig.S.1. (A.): UV -Vis data for self-degradation of *o-DCB* in visible light irradiation; **(B)** Adsorption of *o-DCB* over BSN-CN-15 in dark; **(C)** Adsorption of *o-DCB* over BSN-CN-1 in dark

The adsorption of *o-DCB* in absence of irradiation for the all the photocatalyst has been performed for almost the same time the photocatalytic reaction is performed and the representative adsorption profile is presented for BSN-CN-15 and BSN-CN-1. It is noticed that effect of adsorption over these catalytic surfaces are nominal. Therefore, as the effect of the adsorption is not such strong for most of photocatalysts of CN, BSN and BSN-CN heterojunctions the effect of adsorption does not play a very strong role for the catalytic reactions

2. Degradation of *o-DCB* using BSN catalyst in visible light

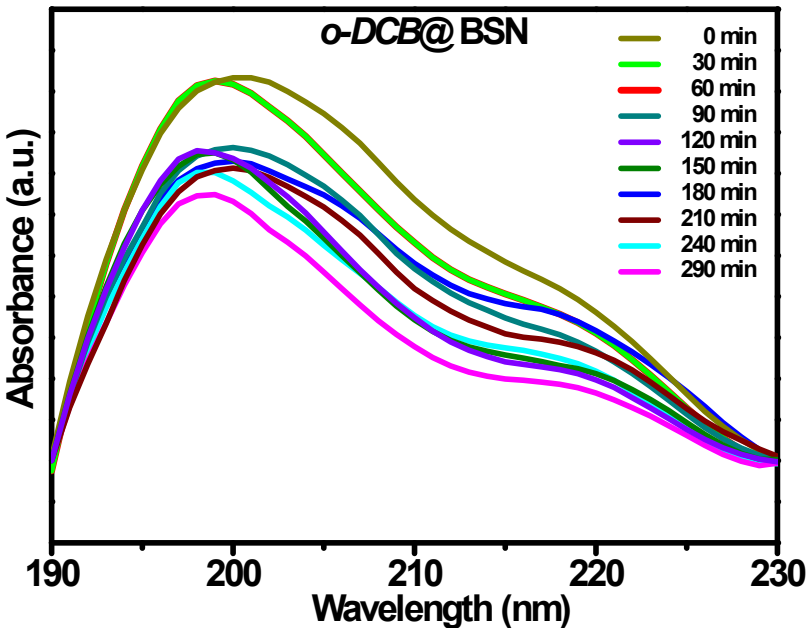


Fig.S.2. UV -Vis data for degradation of *o-DCB* using BSN catalyst in visible light irradiation.

3. Degradation of *o-DCB* using CN catalyst in visible light

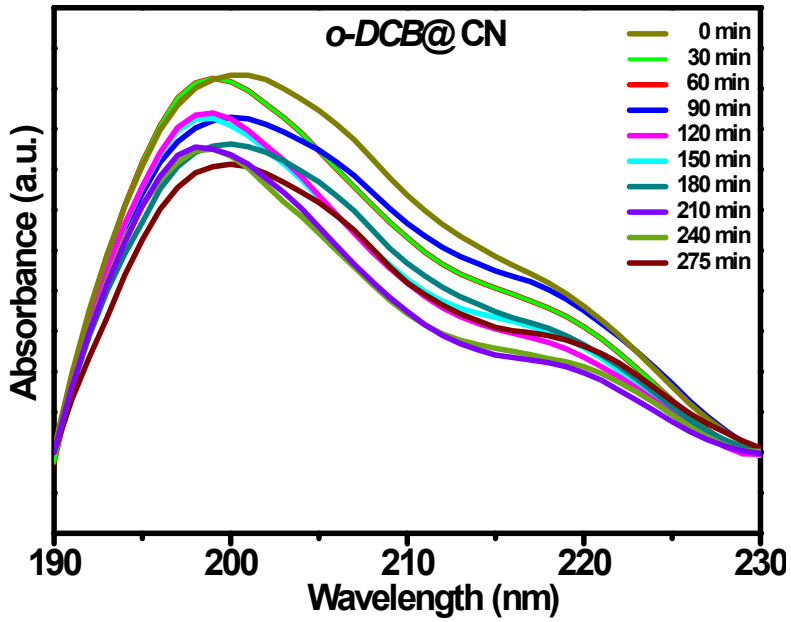


Fig.S.3. UV -Vis data for degradation of *o-DCB* using CN catalyst in visible light irradiation.

4. Degradation of *o-DCB* using BSN-CN-1 catalyst in visible light

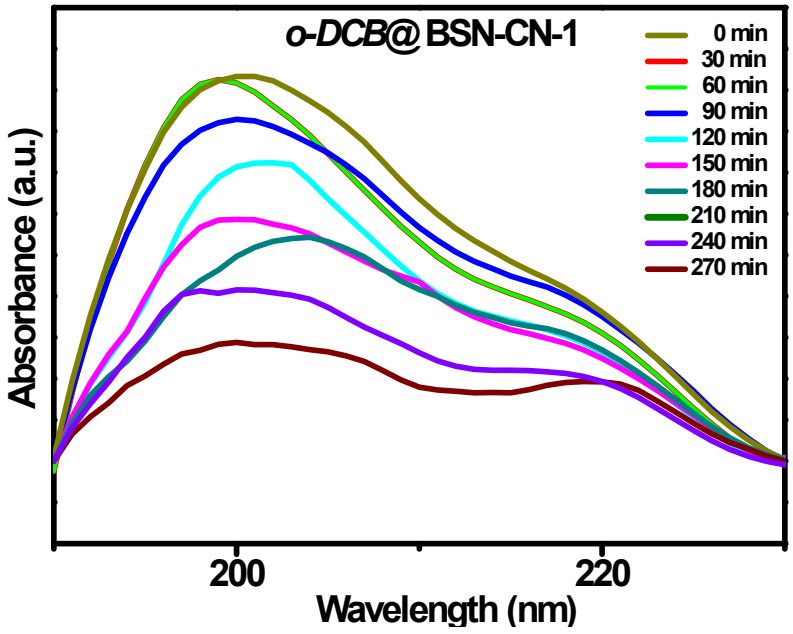


Fig.S.4. UV -Vis data for degradation of *o-DCB* using BSN-CN-1 catalyst in visible light irradiation.

5. Degradation of *o-DCB* using BSN-CN-5 catalyst in visible light

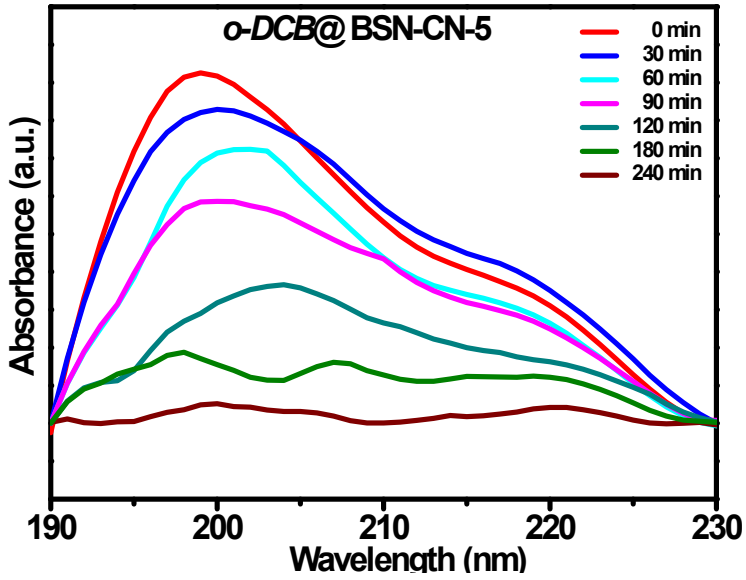


Fig.S.5. UV -Vis data for degradation of *o-DCB* using BSN-CN-5 catalyst in visible light irradiation.

6. Degradation of *o-DCB* using BSN-CN-10 catalyst in visible light

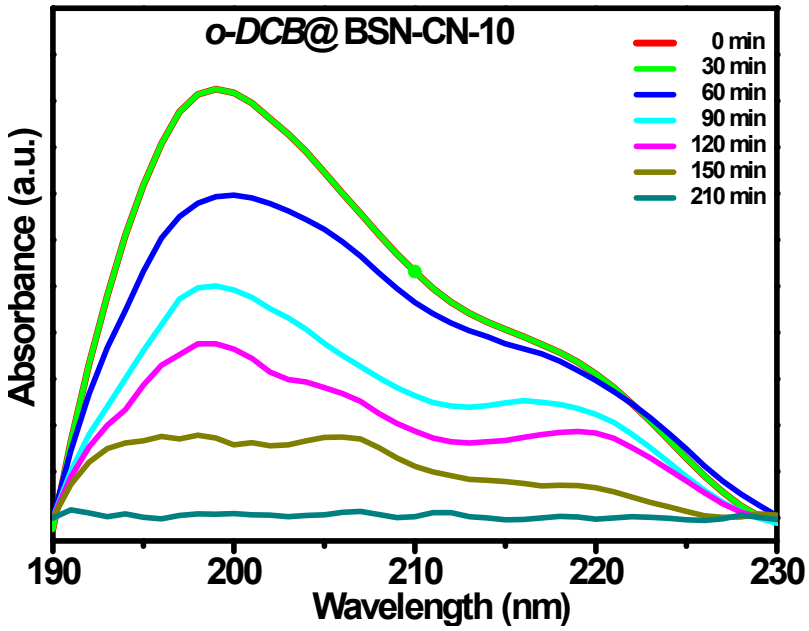


Fig.S.6. UV -Vis data for degradation of *o-DCB* using BSN-CN-10 catalyst in visible light irradiation.

7. Degradation of *o-DCB* using BSN-CN-15 catalyst in visible light

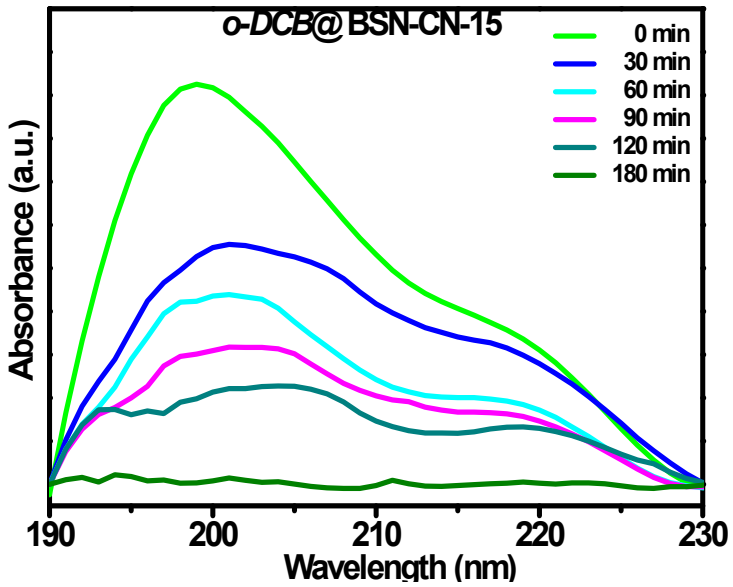


Fig.S.7. UV -Vis data for degradation of *o-DCB* using BSN-CN-15 catalyst in visible light irradiation.

8. CV Data

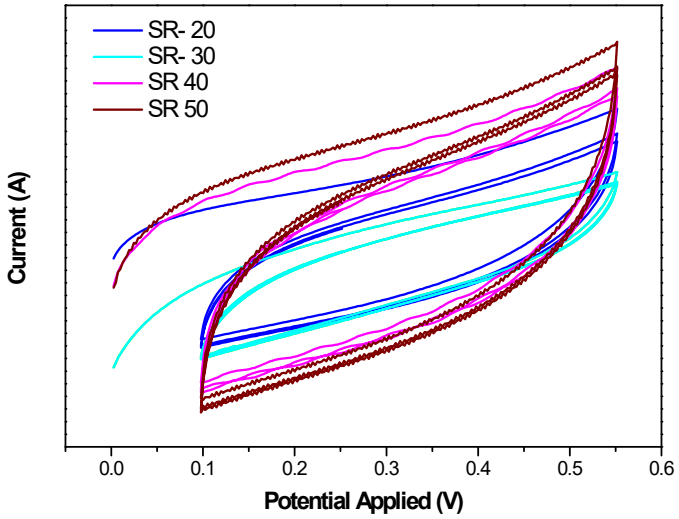


Fig. S-8: CV data for g-C_3N_5 with different scan rates.

9. EDS-Data

Element	Weight (%)	Atomic (%)
C K	1.40	57.00
N K	0.77	27.01
O K	0.51	15.61
Sn L	0.05	0.19
Bi M	0.08	0.19
Total	2.81	-

Table-S.1- EDS data for the BSN-CN-15 photocatalyst.

10. Apparent Quantum Efficiency.

Apparent Quantum Efficiency (AQE) calculation Bi-loaded C_3N_5 photocatalysts

The Apparent Quantum Efficiency (AQE) of the photocatalysts, as detailed in the Supporting Information (SI), demonstrates a clear increase with Bi substitution. 15% BSN-CN exhibited the highest AQE of 0.45%, while $Bi_2Sn_2O_7$ displayed the lowest (0.093%) and CN exhibited the least AQE of 0.080%. This trend suggests a systematic enhancement in AQE with % dispersion of BSN-CN. The tabulated AQE values for all photocatalysts are provided in Table-S-X (S.I.).

AQE of $Bi_2Sn_2O_7$

Apparent quantum Efficiency (AQE) is defined as the ratio of number of reacted electrons to the number of incident photons. The general equation is given as below (1, 2, 3, 4)

$$AQE = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100 \qquad \text{…….…. (5)}$$

As given in equation (1), during the photocatalytic *o-DCB* oxidation, stoichimetrically 2, electrons are required to produce one molecule of CO_2. Though this reaction is a multistep reaction and to be checked which is the slowest, however generically each step being a 2 electrons step will mostly a two electron step.

$$3C_6H_4Cl_2 + 39/2\ O_2 \longrightarrow 18\ CO_2 + 6\ H_2O + 3HCl \qquad \text{…… (6)}$$

Therefore, number of reacted electrons can be calculated by directly multiplying 2 with mole of CO_2 produced during the photocatalytic reaction.

Number of reacted electrons= [P.F] x 2 x N_A …… (7)

Where, [P.F] = Percent Product fomed from $3.3x10^{-5}$ molar solution in time (*t*)
& N_A = Avogadro's number (6.022×10^{23} mol^{-1})

$[P.F]_{Bi2Sn2O7}$ = 30% (in 290 min)

$= 0.30 \times 3.3 \times 10^{-5} \times 6.023 \times 10^{23}$

$= 5.96 \times 10^{18}$

Therefore,

No. of Reacted electrons = $2 \times 5.96 \times 10^{18}$

$= 11.92 \times 10^{18}$

Now, No. of photons = $\frac{Light\ absorbed\ by\ the\ photocatalyst}{The\ average\ photon\ energy}$ x t ..... (8)

Where; t= time taken for the reaction

Light Absorbed by the photocatalyst = H x A

H= Input from the Source of the Light=234 mW/cm^2 = 2340W/m^2

A= Illuminated Geometrical Surface Area of the Reactor Used = Illuminated Geometric irradiation area of the photocatalyst placed inside the photo-reactor = 0.00049 m^2 = 50% of the Geometric Surface area of the used reactor (Reference by Grätzel *et al.*)

Light absorbed by the photocatalyst= 2340 x 0.00049= 1.14 J/sec

The average photon energy = $\frac{hc}{\lambda}$

h =Planck's constant= 6.626 x 10^{-34} Jsec; c = velocity of light =3 x 10^8 m/sec

λ = Maximum Emission Wavelength for the spectrum of the Source = 430 nm= 430 x 10^{-9} m

The average photon energy= 4.62 x 10^{-19}

Therefore,

No. of Photons = 1.14 / 4.62 x 10^{-19} x 290 x 60

= 4293 x 10^{19}

= 4.29 x 10^{22} photons

AQE= $\frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons}$ x 100

= 11.93 x 10^{18}/4.29 X 10^{22} x 100

= 0. 027 %.

The above calculated Quantum Efficiency is the Apparent Quantum Efficiency= AQE of $Bi_2Sn_2O_7$.

AQE of C_3N_5

[P.F] $_{C3N5}$ = 36% (in 275 min)

$$AQE = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100 \quad \text{..... (9)}$$

As given in equation (1), during the photocatalytic *o-DCB* oxidation, stoichimetrically 2, electrons are required to produce one molecule of CO_2. Though, this reaction is a multistep reaction as shown in the formation of the intermediates (and to be checked which is the slowest to determine the R.D.S.), however generically each step being a two electron step will mostly a two electron step.

$[P.F]_{C3N5}$= 36% (in 275 min)

$= 0.36 \times 3.3 \times 10^{-5} \times 6.023 \times 10^{23}$

$= 7.15 \times 10^{18}$

No. of Reacted electrons = $2 \times 7.15 \times 10^{18}$

$= 14.30 \times 10^{18}$

No. of Photons= $1.14 / 4.62 \times 10^{-19} \times 275 \times 60$

$= 4071.43 \times 10^{19}$ photons

$= 4.07 \times 10^{22}$ photons

AQE = $14.30 \times 10^{18} / 4.07 \times 10^{22} \times 100$

$= 3.513 \times 10^{-2}$

= 0.035%

AQE of BSN-CN-1

$[P.F]_{BSN\text{-}CN\text{-}1}$ = 80% (in 270 min)

$$AQE = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100 \quad \text{..... (10)}$$

As given in equation (1), during the photocatalytic *o-DCB* oxidation, stoichimetrically 2, electrons are required to produce one molecule of CO_2. Though this reaction is a multistep reaction as shown in the formation of the intermediates (and to be checked which is the slowest to determine the R.D step), however generically each step being a two electron step will mostly a two electron step.

[P.F] $_{BSN\text{-}CN\text{-}1}$ = 80% (in 270 min)

= 0.80 X 3.3 X 10^{-5} X 6.023 X 10^{23}

= 15.90 x 10^{18}

= 1.590 x 10^{19}

No. of Reacted electrons = 2 x 1.590 x 10^{19}

= 3.18 x10^{19}

No. of Photons = 1.14 / 4.62 x 10^{-19} x 270 x 60

= 3997.40 x 10^{19} photons

= 3.997x 10^{22} photons

AQE = 3.180 x 10^{19}/3.997x10^{22} x100

= 0.80 x 10^{-1}

= 0.08%

AQE of BSN-CN-5

[P.F] $_{BSN\text{-}CN\text{-}5}$= 93 % (in 240 min)

$$AQE = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

As given in equation (1), during the photocatalytic *o-DCB* oxidation, stoichimetrically 2, electrons are required to produce one molecule of CO_2. Though, this reaction is a multistep reaction as shown in the formation of the intermediates (and to be checked which is the slowest to determine the R.D.S.), however generically each step being a 2 electron step will mostly a two electron step.

[P.F] $_{BSN\text{-}CN\text{-}5=}$ 93% (in 240 min)

= 0.93 X 3.3 X 10^{-5} X 6.023 X 10^{23}

= 18.48 x 10^{18}

= 1.848 x 10^{19}

No. of Reacted electrons = 2 x 1.848 x 10^{19}

$= 3.696 \times 10^{19}$

No. of Photons = $1.14 / 4.62 \times 10^{-19} \times 240 \times 60$

$= 3553.24 \times 10^{19}$ photons

$= 3.553 \times 10^{22}$ photons

AQE= $3.696 \times 10^{19}/3.553 \times 10^{22} \times 100$

$= 1.040 \times 10^{-1}$

$= 0.10\%$

AQE of BSN-CN-10

$[P.F]_{BSN\text{-}CN\text{-}10} = 99\ \%$ (in 210 min)

$$AQE = \frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

As given in equation (1), during the photocatalytic *o-DCB* oxidation, stoichimetrically 2, electrons are required to produce one molecule of CO_2. Though, this reaction is a multistep reaction as shown in the formation of the intermediates (and to be checked which is the slowest to determine the R.D.S.), however generically each step being a 2 electron step will mostly a two electron step.

$[P.F]_{BSN\text{-}CN\text{-}10=}$ 99% (in 210 min)

$= 0.99 \times 3.3 \times 10^{-5} \times 6.023 \times 10^{23}$

$= 19.87 \times 10^{18}$

$= 1.987 \times 10^{19}$

No. of Reacted electrons = $2 \times 1.987 \times 10^{19}$

$= 3.974 \times 10^{19}$

No. of Photons = $1.14 / 4.62 \times 10^{-19} \times 210 \times 60$

$= 3109.09 \times 10^{19}$ photons

$= 3.109 \times 10^{22}$ photons

AQE= $3.974 \times 10^{19}/3.109 \times 10^{22} \times 100$

= 1.278 x 10^{-1}

= 0.12%

AQE of BSN-CN-15

[P.F] $_{BSN\text{-}CN\text{-}15}$= 99.9 % (in 180 min)

AQE= $\frac{Number\ of\ reacted\ electrons}{Number\ of\ incident\ photons}$ x 100 ……. (11)

As given in equation (1), during the photocatalytic *o-DCB* oxidation, stoichimetrically 2, electrons are required to produce one molecule of CO_2. Though, this reaction is a multistep reaction as shown in the formation of the intermediates (and to be checked which is the slowest to determine the R.D.S.), however generically each step being a 2 electron step will mostly a two electron step.

[P.F] $_{BSN\text{-}CN\text{-}15=}$ 99.9% (in 180 min)

= 0.999 X 3.3 X 10^{-5} X 6.023 X 10^{23}

= 19.87 x 10^{18}

= 1.987 x 10^{19}

No. of Reacted electrons = 2 x 1.987 x 10^{19}

= 3.974 x10^{19}

No. of Photons = 1.14 / 4.62 x 10^{-19} x 180 x 60

= 2664.93 x 10^{19} photons

= 2.664 x 10^{22} photons

AQE= 3.974 x 10^{19}/2.664 x 10^{22} x 100

= 1.491 x 10^{-1}

= 0.14%

Catalysts	**AQE (%)**
BSN	0.027
CN	0.035
BSN-CN-1	0.08

BSN-CN-5	0.10
BSN-CN-10	0.12
BSN-CN-15	0.14

Table S-2: Calculated Apparent Quantum efficiencies of different photocatalysts.

10. Complete mineralization of *o-DCB* with different photocatalysts and Mass spectroscopic evaluation in closed photocatalytic reactor.

We conducted photocatalytic mineralization experiments in a 90 ml closed quartz reactor (Fig. S-8), fitted with a glass valve for evacuating the system. For each run, we introduced 60 ml of *o-DCB* solution (initial concentration 3.3×10^{-5} mol/dm^3, pH around 6.7) and 100 mg of the photocatalytic material. Reaction progress was tracked using an Extorr RGA quadruple mass spectrometer, capable of detecting masses from 1 to 200. This monitoring occurred under vacuum conditions of 10^{-7} mbar, with a sample pressure of 10^{-6} mbar. Prior to data collection, we obtained baseline mass spectra of air. We then established CO_2 calibration curves by preparing various CO_2 air mixtures in an evacuated glass bulb. These three distinct calibration curves, tailored for different concentration ranges, were linearly fitted using ORIGIN software, yielding an adjusted R^2 value of approximately 0.998.

Fig.S.9. The experiments have been conducted in the above photocatalytic reactor.

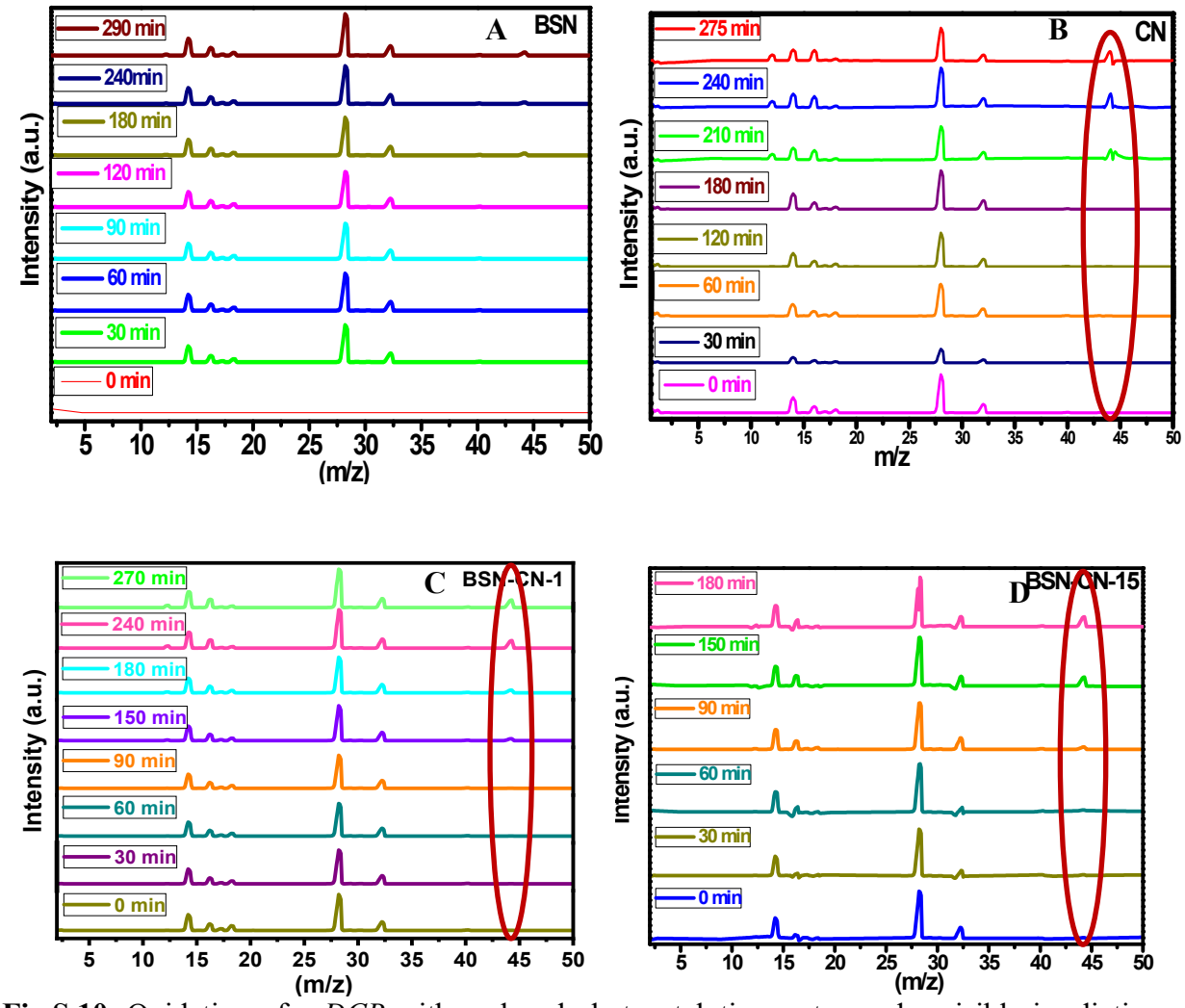


Fig.S.10. Oxidation of *o-DCB* with a closed photocatalytic reactor under visible irradiation using (A) BSN; (B) CN; (C) BSN-CN-1; (D) BSN-CN-15 -photocatalysts and the product being studied with the mass spectroscopy.

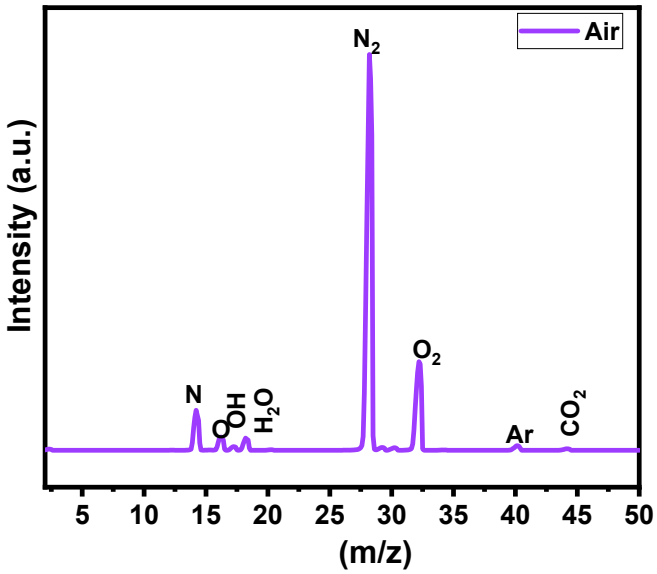


Fig. S.11. Mass spectra of atmospheric air.

Volume of CO_2 formed analysed from the calibration curve from the mass spectroscopic data =A

Amount of CO_2 to be formed stoichimetrically from the volume of *o-DCB* present where it is completely oxidised to CO_2 = B

$$\text{Percentage of product formed } (CO_2\,\%) = \frac{A}{B} \text{ x } 100 \quad \ldots\ldots\ldots (12)$$

11. Catalytic recyclability:

Catalytic recyclability has been tested for four consecutive cycles and there is slight lowering in the catalytic efficacy as a function of the recyclability that has been shown in the **Fig.11.C**. The catalytic efficiency increases after heat treatment of the catalysts @ 100 °C in air.

12. Calculation of Strain in the BSN as a function of temperature.

In order to calculate the strain, the BSN-CN-15 samples as a function of heating initially the XRD for (1h) duration (Fig.S-14) for each sample was obtained. Through rietveld refinement was performed to calculate the lattice parameters as well as the broadening; which was later plotted in the Fig.S-15 to obtain the lattice strain as per the Williamson Hall equation -1.

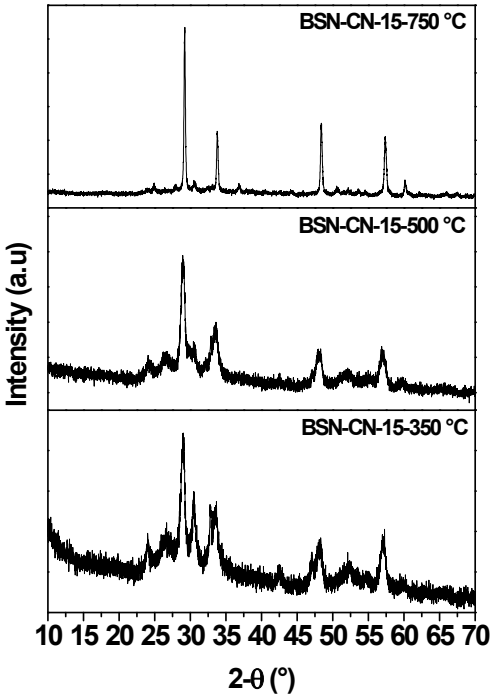


Fig.S-12: Long time XRD (1h) of the BSN-CN-15 as a function of temperature the a) 350 °C; b) 500 °C & c) 750 °C.

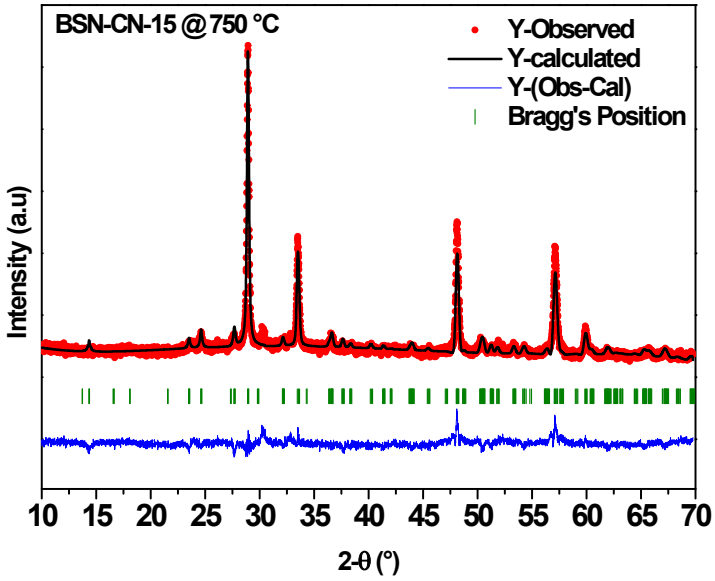
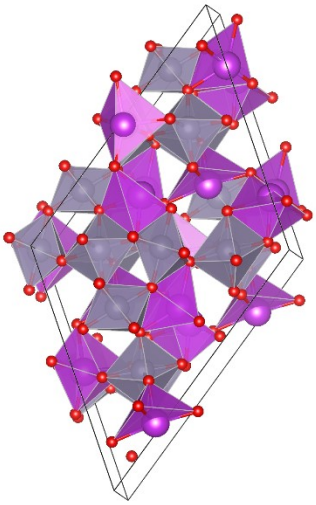


Fig.S-13: Rietveld Refinement plot for BSN-CN-15 -750 °C



Scheme-1: C1c1 Monoclinic $Bi_2Sn_2O_7$ with lattice parameter of (a= 13.15; b= 7.54; c= 16.01) and (α= β= 90°); (γ=125.012°):- ICSD- 239965.

The contribution from the crystallite size and strain could be delineated by using Williamson-Hall equation (eqn.-1).

$$\mathbf{B\cos\theta = 0.9\lambda/t + \eta \sin\theta} \quad \text{..... [13]}$$

where,

B = Broadening (in radian) as calculated from Rietveld Refinement,
t = crystallite size & $\eta = 4\varepsilon$ (ε=Strain)

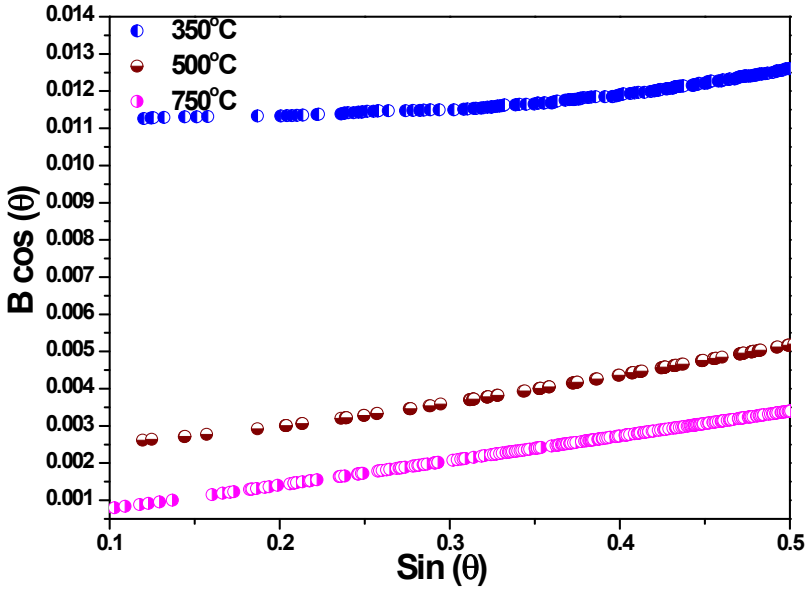


Fig. S-14: Williamson Hall plot to determine strain calculation (In equation 13)

13. Crystallographic understanding of the HRTEM images of the BSN-CN samples.

Sample	1/2r (nm^{-1})	1/r (nm^{-1})	r(nm)	d-spacing (Å)	(hkl)
BSN-CN-15	6.3	3.15	0.317460317	3.174603175	6 2 2
	14.123	7.0615	0.141612972	1.416129717	8 12 4
	17.121	8.5605	0.116815607	1.168156066	12 3 2

Table-S-3: SAED Pattern calculation of the Fig.2.A (BSN-CN-15) showing the different planes as compared to the ICSD-File-239965

Sample	1/2r (nm^{-1})	1/r (nm^{-1})	r(nm)	d-spacing (Å)	(hkl)
BSN-CN-1	7.695	3.8475	0.259909032	2.599090318	0 0 4
	9.134	4.567	0.21896212	2.189621196	2 2 4
	11.912	5.956	0.167897918	1.678979181	2 6 2

Table-S-4: SAED Pattern calculation of the Fig.2.B (BSN-CN-15) showing the different planes as compared to the ICSD-File-239965

14. **Elemental Analysis from XPS for the photocatalysts and used photocatalysts.**

BSN (Elements)	**Atom (%)**	**FWHM**	**Atom (%) after reaction**	**FWHM**
Bi	15.34	2.24	15.89	2.04
Sn	22.37	2.35	21.48	2.24
O	62.69	3.5	62.63	3.61

Table-S-5: Elemental analysis from XPS of the BSN sample before and after catalysis.

BSN-CN-15 (Elements)	**Atom (%)**	**FWHM**	**Atom (%) after reaction**	**FWHM**
Bi	1.34	2.24	1.27	2.04
Sn	1.37	2.35	1.47	2.24
O	14.13	3.5	13.79	3.61
C	29.23	2.7	31.51	3.1
N	53.96	2.05	51.96	2.5

Table-S-6: Elemental analysis from XPS of the BSN-CN-15 sample before and after catalysis

15. **SEM of the used sample after catalysis**.

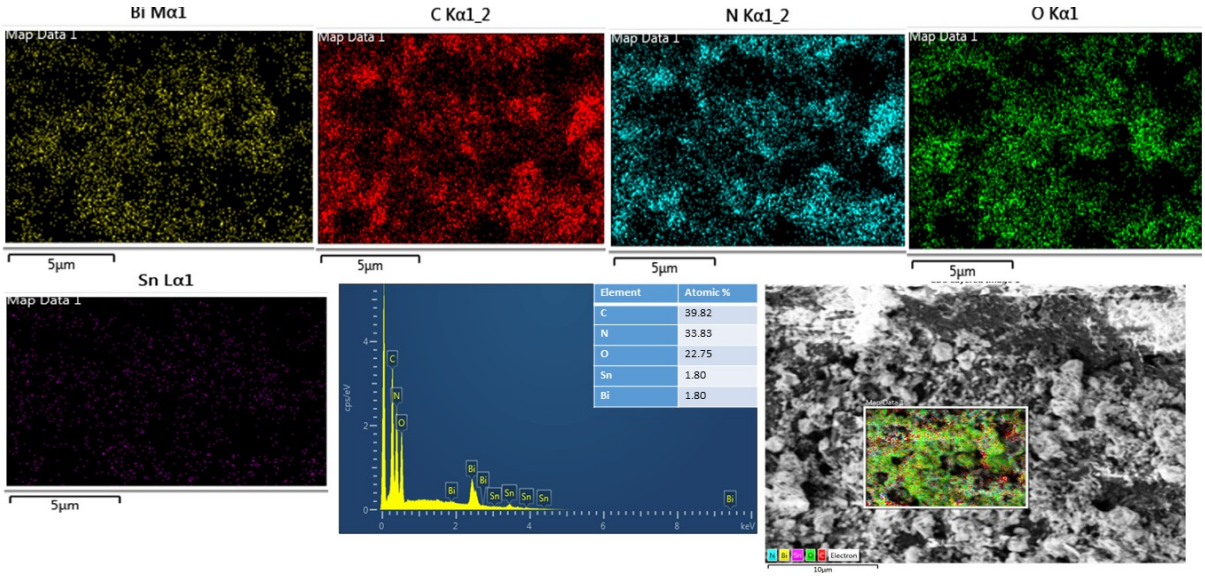


Fig.S-15: SEM image for the used BSN-CN-15 samples with elemental mapping for the different elements (a) Bi-Mα;(b) C-Kα;(c) N-Kα;(d) O-Kα;(e) Sn-Lα(f) EDS spectra for the required sample.

The elemental percentage as obtained from the EDS analysis is presented below along with that of the comparison for the same sample before catalysis.

After Catalysis [a]		**Before Catalysis [b]**	
Element	**Atomic %**	**Element**	**Atomic %**
C	39.82	C	37.82
N	33.83	N	35.83
O	22.75	O	22.81
Sn	1.80	Sn	1.73
Bi	1.80	Bi	1.81
Total	100.00	Total	100.00

Table:S-7: Elemental analysis form the EDS analysis of the a) BSN-CN-15 -After catalysis from Fig.S-15.f and b) BSN-CN-15-sample before catalysis Fig.3.C.

This show there is generically no leaching of the BSN elements post catalysis as can be understood both from the SEM-EDS analysis and the of the XPS elemental analysis and it should be so as the heterojunction is formed with tetragonal BSN ($Bi_2Sn_2O_7$) and that of g-C_3N_5, thereby leaching of the Bi or will change the phase altogether for BSN. Thereby no alteration in the Bi:Sn:O ratio post catalysis confirms the fact that the phase entity remains intact even after photocatalysis for these heterojunctions.