Modification of SnO_2 nanotubes with g-C_3N_4 for superior photocatalytic degradation of toxic dye under visible light irradiations

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Submitted by

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Certificate

I hereby certify that the work presented in this thesis entitled "**Modification of SnO_2 nanotubes with g-C_3N_4 for superior photocatalytic degradation of toxic dye under visible light irradiations** " submitted in partial fulfilment of the requirements for the award of degree of Master of Science in Chemistry submitted to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is an authentic record of my own work carried out under the supervision of Dr.Soumen Basu . The matter embodied in the **thesis** has not been submitted to any other University for the award of any other degree or diploma. Works of other authors cited in this thesis have been duly acknowledged under reference section of this thesis.

Date: 29/6/18.

Pooja Kumari
Pooja Kumari

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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ABSTRACT

The industrial and domestic waste water effluents from any sources include organic chemicals and pathogens; have maximum pollutants, which can be removed before discharging into water bodies. One of the major water contaminated pollutant has been measured as Rhodamine B. Such pollutant is leading in surface water and groundwater. It will cause irreversible hazards to human and aquatic life in present era. Nanotechnology plays a main role in degrading such type of pollutant. In order to fulfill today's requirement, we have decided to handle the eco-friendly green synthesis of nanoparicles and its application by merging important fields like environmental sciences, chemical sciences and biotechnology. Here our work emphasizes on the single step synthesis of SnO_2/ C_3N_4 nanoparticles and it was confirmed by various physico-chemical characterization techniques such as UV-Visible spectroscopy, XRD, TEM, SEM and BET surface area. This nano-composite showed the excellent photocatalytic activity that is 97 % and making it promising photocatalysts for degradation of dyes.

Chapter 1 INTRODUCTION

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List of Abbreviations

SnO_2	Stannous oxide
NPs	Nanoparticles
CB	Conductance band
VB	Valence band
UV	Ultraviolet
Wt %	Weight percent
g-C_3N_4	Graphitic carbon nitride
TEM	Transmission electron microscopy
SEM	Scanning electron microscope
EDX	Energy dispersive X-ray
NH_3	Ammonia
XRD	X-ray diffraction
BET	Brunauer- Emmett-Teller
NC	Nanocomposite

List of Symbols

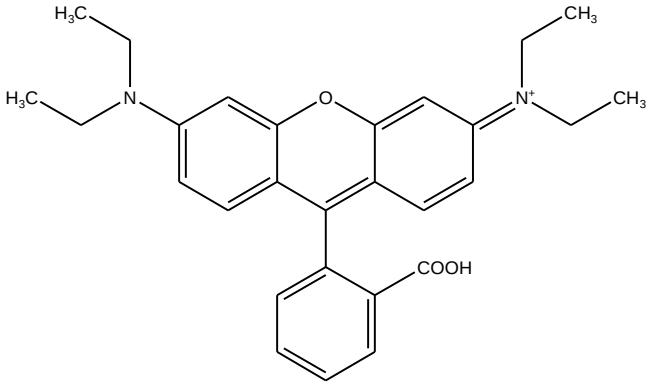
kV	Kilo Volt
Mg	Milli gram
Ml	Milli liter
IR	Infrared
µL	Micro liter
e^-	Electron
h^+	Hole
min	Minute
eV	Electron Volt
a.u.	Arbitrary unit
λ_{ex}	Excitation wavelength
E_g	Energy Gap

CHAPTER 1 : Introduction

1.1 Water is essential for human being

As stipulated in [1] of South African constitution ; where it state that everybody has the privilege to adequate water, yet a few people are as yet denied of this need. South Africa is a water rare nation and different methodologies are being defined to attempt and save the water still accessible. As indicated by the World bank, South Africa has yearly normal precipitation of 495 mm inside and out. As indicated by UN insights, of the 51 million individuals in South Africa, around 60% live in urban zones and the staying 40% constitutes individuals in provincial zones. The nation relies upon 77% surface water, 9% groundwater and 14% reused water. In any case, the populace's reliance on water isn't equitably conveyed.

Various industries use coloring matter as well as dyes for the shading of their items ,for example rubber, textiles, cosmetics .Research has demonstrated that more than 15% of the entire dye is lost untreated in effluents representing a risk to the well-being and general prosperity of mankind and nature[2]. Currently organic treatment forms don't sufficiently treat dye waste water [3] because of the low biodegradability. [4] The natural poisons in the wastewater are very harmful and they can deliver some potential cancer-causing agents, that will be hurtful to the people and creatures and in addition the entire ecosystems. [5] Among numerous potential answers for this issue, the photo catalysis has developed as a interesting procedure since it is financial, nontoxic and inexhaustible. [6-8]



Rhodamine B
($C_{28}H_{31}ClN_2O_3$)

1.2 Dyes

Dyes can be described as- formed colors by changing the structure when applied to the substrate. These are classified by their synthetic structures, applications. The present study target on Rhodamine B (dye). This is generally utilized as a colorant in materials and is a decent water tracer fluorescent [9]. It is unsafe and poisonous to people and causes aggravation of the skin, eyes and respiratory tract,the cancer-causing nature, and neurotoxicity toward living creatures [10, 11]. It is possible to degrade the dye with the help of photo catalysts under visible light due to their absorption in visible range [12, 13]. In this investigation, photo catalytic action on RhB dye by SnO_2 photo catalyst by sunlight based light illumination was considered. The response of catalyst and the concentration of RhB on the photocatalytic impact was researched.

1.3 What is catalyst

Catalysis is a phenomenon that accelerate the chemical reaction and coming back to its original state by altering the rate of reaction. Its characteristics are as follows:-

- The catalyst provides an alternative which is energetically favourable.
- Activation energy for the catalyzed reactions are more as compared to the uncatalyzed reaction.
- Catalyst does not change the equilibrium constant.
- Catalyst speeds up the reaction to the same extent (i.e. in both forward and backward direction.)
- Catalyst can be Atoms, Molecules and solid surfaces.

Catalysts arrive in a huge number of structures ranging from particles and atoms to extensive structures, for example Zeolites and compounds. They might be utilized in environment in fluids, gases or at the surface of solids.

1.4 Why is catalyst important?

In twentieth century reactions can be controlled on the basis of temperature, weight and contact time. Raising the temperature and weight will empower stoichemetric responses to continue at a sensible rate of generation, yet the reactors in which such conditions can be

securely kept up turned out to be dynamically more costly and hard to make furthermore, there are thermodynamic restrictions to the conditions under which items can be shaped for eg. The transformation of N_2 and H_2 into ammonia is impossible above 650^0 C. Without catalysts some common reactions would not be possible. Catalysts speed up the reactions under the favourable thermodynamic condition at much lower pressure and temperature.

1.5 Catalyst in Industries

There are many functions of catalysts in the preparation of chemicals in industries. Catalysts consist of D-block metals which are of great applications to the industry. Roughly 86 to 90% products of chemical industries are formed in catalytic methods. Catalysts permit industrially necessary reactions to be completed effectively under basically achievable conditions by speeding up the reactions. Catalysts are the workhorses of chemical conversions in the industry. Catalysts are used precisely and reduce the waste production. Catalysts are essential in

- Production of transportation fuels and solid chemicals all over the world.
- To prevent pollution by avoiding formation of bio products.
- Reduction of contamination in end-of-pipe solutions (automotive and industrial exhaust).

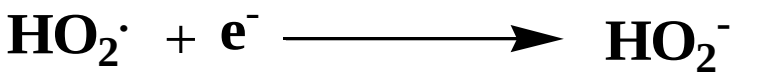
1.6 Photocatalyst

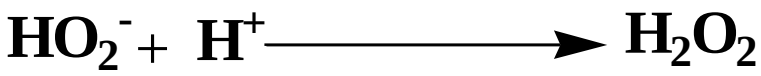
Photocatalyst is a easy method to resolve contamination from environment since it provides a practical pathway to drive synthetic responses. Semiconductor based catalyst, which is a potential way to deal the environment pollution has attracted more interest. In the presence of catalyst, Photocatalysis is the accelerating of a photoreaction. Due to the contamination in water photocatalytic methods has been used. [14] Photocatalysis use semiconductors to enhance its activity. Photo-excitation of the semiconductor is given below;

$$O_2 + e^- \longrightarrow O_2^{\cdot -}$$

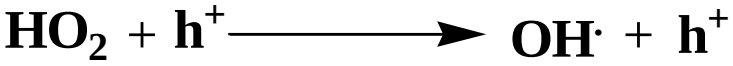
$$HO_2^- + H^+ \longrightarrow H_2O_2$$

In this method we can prevent the hole recombination.





Photogenerated holes react to water molecule to give $OH^{\cdot}$



1.7 Nanotechnology and Nanoparticles.

Nanotechnology is the research of very small particles. It unites analysis and engineering from a wide range of subjects, for eg. Applied physics, supramolecular chemistry and material sciences. Nanoparticles (1-100 nm in measure) have an extraordinary place in nano-sciences and nanotechnology; they are very small material having size reaching from 1 to 100 nm. They can be ordered into various classes by virtue of their properties, shapes or sizes. As indicated by the United States National Nanotechnology initiative, "Nanotechnology is a science, designing, and innovation directed at the nanoscale, which is around 1 to 100 nanometres". One nanometre is a billionth of a meter. Researchers are having incredible achievements making material at nanoscale to give greater value to properties such as higher quality, lighter weight, expanded electrical conductivity and synthetic reactivity contrasted with their bigger scale equivalents.

1.8 Metal oxide

A huge attempt has been made in the application and synthesis of metal oxides during the past decade. In areas of chemistry and material sciences metal oxides play a very important role. Due to their limited size they exhibit unique physical and chemical properties.

A perfect metal oxide should possess: a) economical, b) chemically inert, c) photoactive, d) ability to be excited with visible and / or near UV light. Due to low cost, water detoxification [15], CO_2 reduction [16] and organic synthesis [17]. TiO_2 has draw more attention for water splitting. Instead of these advantages it has a fundamental drawbacks:

- Broad band gap and more recombination rate of e^- hole pairs.

So various photocatalytic materials such as metal oxides [18-19], metal halides[20] and metal-free semiconductors[21] have been suggested as alternative for general TiO_2 photocatalysis.

A metal free photocatalyst- graphitic carbon nitride (g-C_3N_4) is reported for hydrogen evolution has attracted more attention [22] in the region of photocatalyst because of its non-toxic nature, high stability[23]. g-C_3N_4 has a high recombination rate, showing its short lifetime and low division effectiveness of photogenerated e^- hole pair , which prompts low quantum efficiency.

Numerous methodologies have been proposed to upgrade the activity of g-C_3N_4 which includes mesoporous g-C_3N_4 to increase the surface area [24], doping it with transition metals [25] and g-C_3N_4 based semiconductors [26,27]. SnO_2 (Stannic oxide) is n-type semiconductor and it was shown that it is less active for the detoxification of water due to its limited band gap (3.60eV) [28].

It was found that the combination of g-$C_3N_4$and SnO_2 will form a new type of (SnO_2/C_3N_4) semiconductor heterojunction with well similar band structure, decreases the e^- hole recombination rate and prolonged the e^- hole pairs lifetime. So new composites were formed with different mass ratio to check the photocatalytic degradation of toxic dye under visible light irradiation.

CHAPTER 2 : Review of literature

Great efforts has been done in the recent years to synthesized the nanocomposite SnO_2/C_3N_4 to enhanced the photocatalytic activity and the degradation of dye under visible light. As we know treatment of industrial waste water has become a major issue. So to remove and clean this organic pollutant from the water is challenge nowdays. Thus different types of nancomposite with g-C_3N_4 are prepared to degrade the dye .One of them is SnO_2/C_3N_4 which shows high efficiency under visible light.

Work done by **Yan et al.** [29] mentioned the preparation of g-C_3N_4 /SnO_2 heterojnction photocatalyst. In this they showed the preparation of g-C_3N_4 /SnO_2 by solvothermal method. For effective charge transfer at the interfaces of nano-composite synergistic effect is considered, O_2 is attributed for the pivotal radical in the dye RhB degradation. The visible active catalyst is powerful catalyst for the treatment of pollution. This work gives a new method for the preparation of g-C_3N_4 based photocatalyst with great application in the area of energy storage, energy conversion, electro catalysis and photo catalysis. SnO_2 shows very less degeradation for RhB,(4.4% degraded in 15 min).While the visible active nanocomposite g-C_3N_4 /SnO_2(4:1) show 97.5%degradation as shown below(already reported)

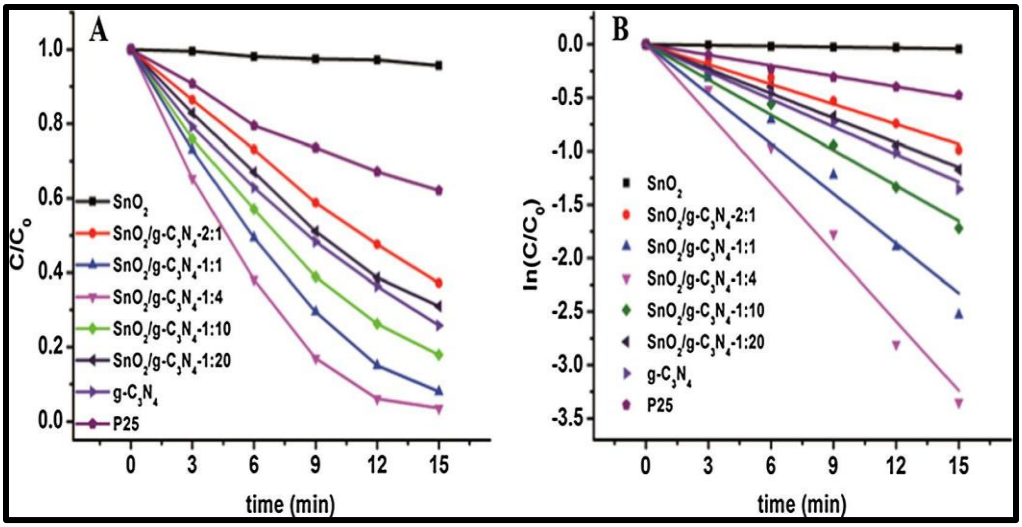


Fig 2 Degradation of RhB under UV-Visible irradiation

In hydrothermal methods by **Xi Chen et al.** g-C_3N_4/ SnO_2 shows enhanced photocatalytic activity. By hydrothermal method different nanocomposite with of g-C_3N_4 are prepared. These

fabricated nano-composite shows the 72.22% (a ,b) degradation efficiency means 17 and 89 times greater than pure of g-C_3N_4 and SnO_2 respectively due to the large surface area and separation efficiency. So the nano-composite of g-C_3N_4 /SnO_2 bacame a promising candidate for the degradation of environment protection and pollutant treatment.

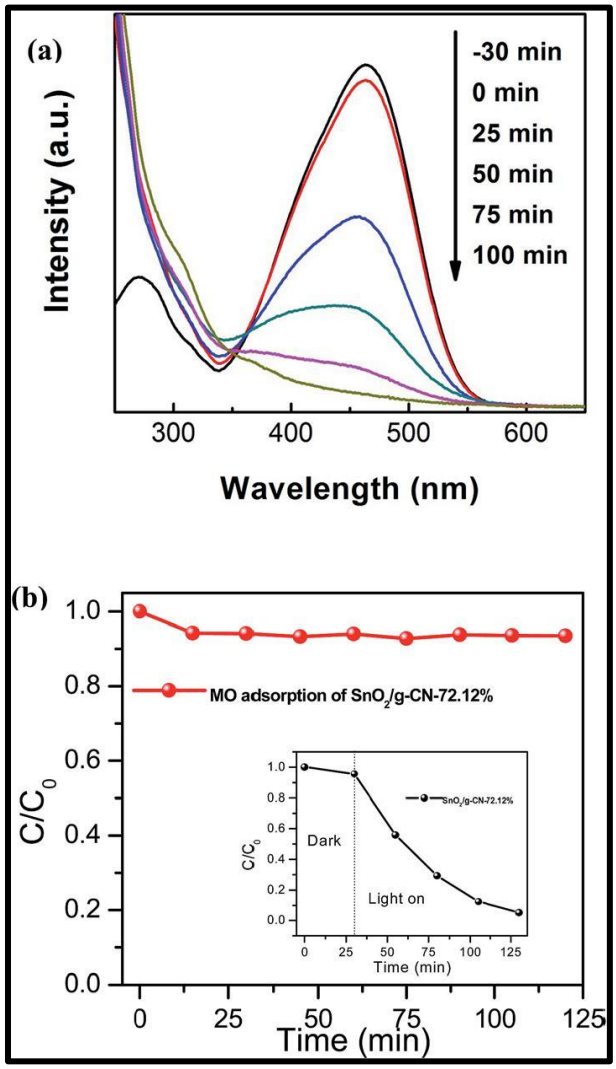


Fig 3 Degradation of dye

A seza et al.[30] stated microwave radiations are appropriate to synthesized the nanocomposite (g-C_3N_4 /SnO_2) by simple pyrolysis the urea with of SnO_2 nanoparticles. To prevent the restacking of SnO_2 nanoparticles are in-situ synthesized and intercalated to the layer of of g-

C_3N_4 .Sheets of g-C_3N_4 are linked to the SnO_2 nanoparticles by hydrogen bond. The nanocomposite prepared by this method enhanced the photocatalytic activity under visible region and efficient catalyst for clean energy formation and water splitting.

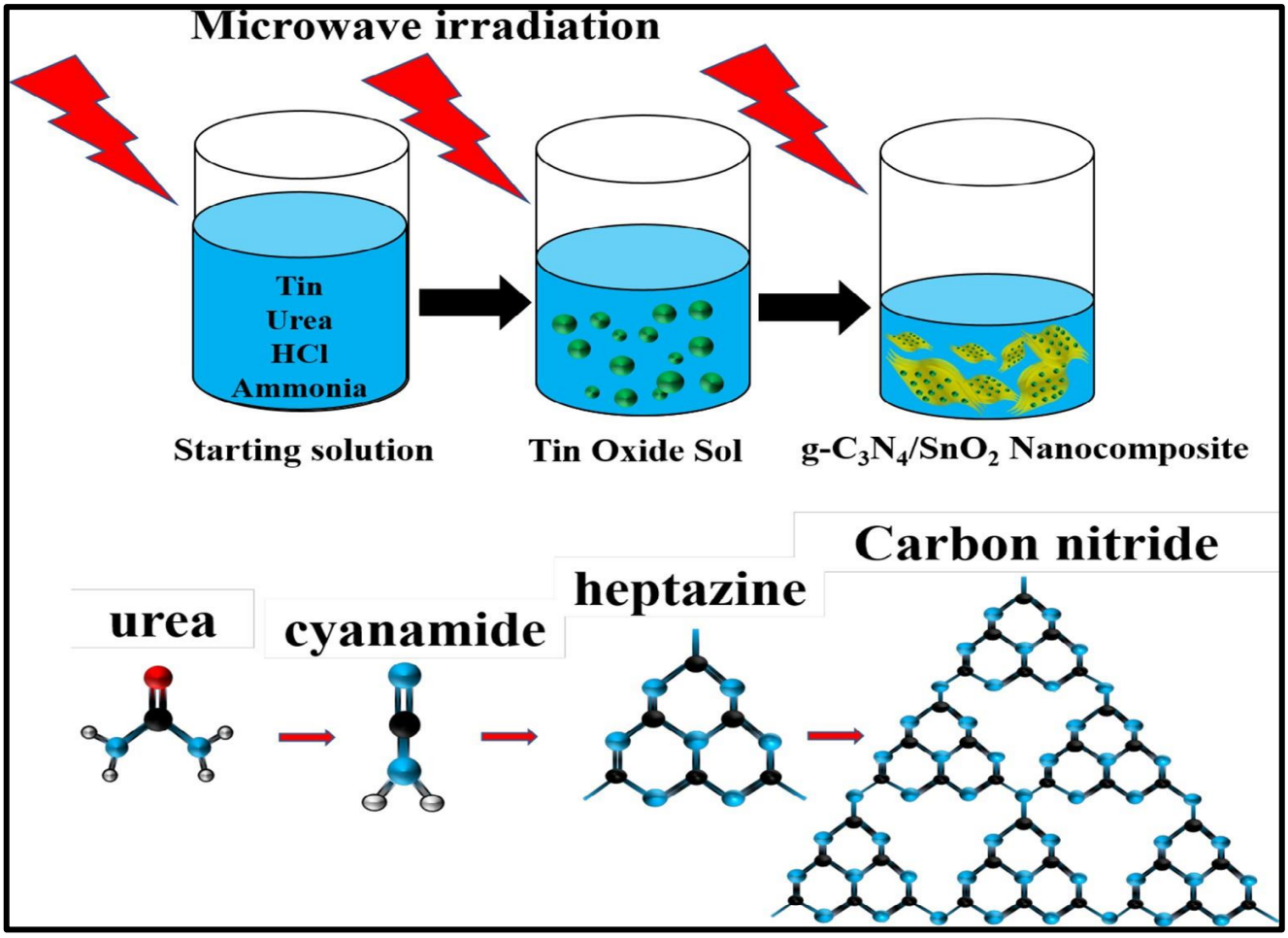


Fig. 4. Scheme for the synthesis of carbon nitride

Kai Li et al. [31] prepared SnO_{2-x}/C_3N_4 nano-sheets by calcination of melamine and Sn $(OH)_4$ in one step. In this paper they studied that, under well-designed conditions the aggregates of g-C_3N_4 are quenched and production of O_{vs} is enhanced. The PEC and Pc activites under visible-LED of reduced nanocomposite are proved to be higher than that of pure g- C_3N_4 and SnO_2.

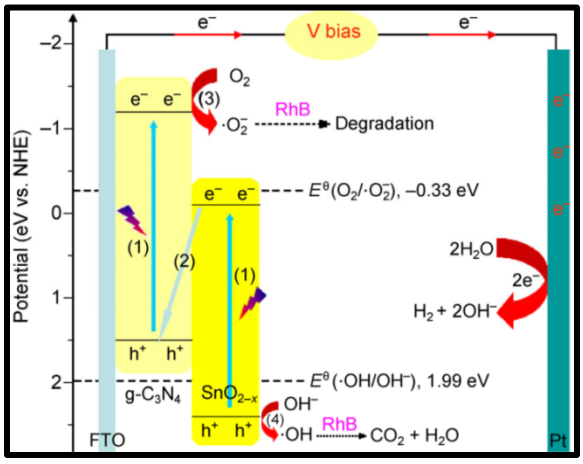


Figure 5 Scheme for electron- hole migration

Rong Yin et al.[32] prepared photocatalyst g-C_3N_4/SnO_2 by ultrasonic assisting deposition method. Nanoparticles of SnO_2 with particle size 2-3 nm are dispersed to the surface of g-C_3N_4.

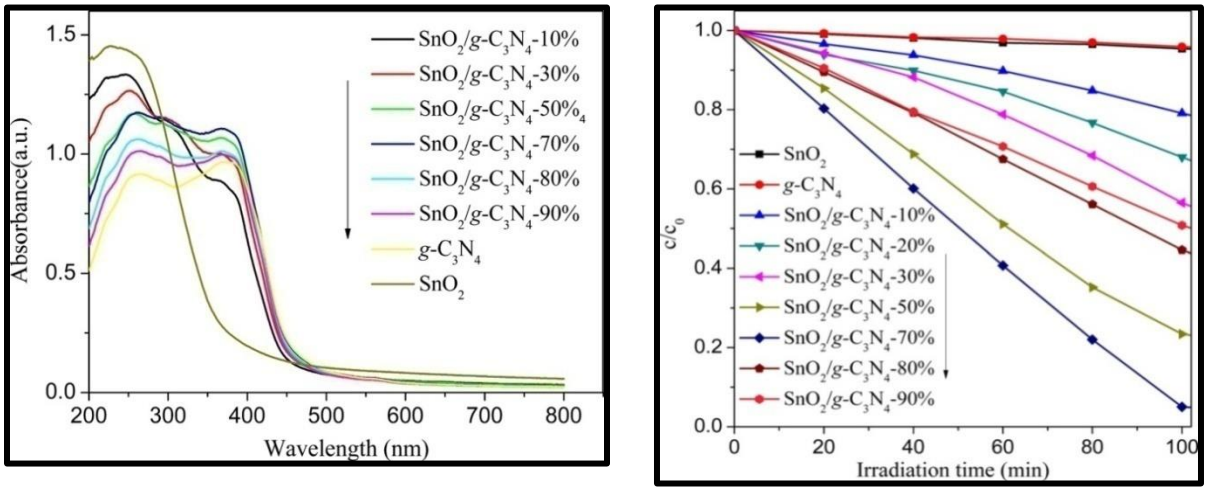


Fig 6 Degradation of MO in the presence of g-SnO_2/g-C_3N_4

They studied that the prepared nanocomposite show high visible activity than pure SnO_2 and g-C_3N_4 and possess good stability. g-C_3N_4 /SnO_2 has highest photocatalytic activity that is 70% under visible light and act as a good catalyst for the reduction of organic waste in air or water.

Pham Van viet et al.[33] stated that the Nano-particles of SnO_2 with size 3 nm are synthesized by hydrothermal method from hydrazine hydrate , $SnCl_2$ and NaOH. Under visible light the nano-particles of SnO_2 with Methylene blue (MB) show high degradation (> 75%) after 15 min and under sunlight 79.26% of dye (MB) degradation take place within 90 min.

Cong qin et al. showed that [34] SnO_2/g-C_3N_4 nano-particles are synthesized by grinding treatment to sense the ethanol gas. In this paper they showed that the nano-composite formed by this method has enhanced the gas sensing properties than the pure SnO_2 and g-C_3N_4.

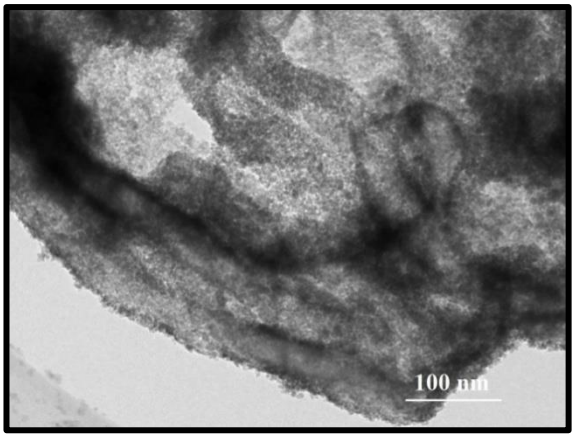


Figure7. TEM image of SnO_2/g-C_3N_4

This is due to the large surface area. So the nanocomposite has high performance ethanol gas sensing properties. TEM images clearly that SnO_2 nanoparticles are dispersed on the surface of g-C_3N_4 and act as a excellent method for sense the ethanol gas.

Vien vo et al. [35] prepared the nanosheets of SnO_2 with g-C_3N_4 and the formed composite is SN/CN, SnO_2 nanosheets are completely dispersed on the surface of g-C_3N_4.The prepared composite that is SN/CN showed high cyclying performance as compare to SnO_2 and g-C_3N_4.

The prepared SnO_2 nanosheets are very thin with thickness range is 20-25 nm, form cauliflower shaped structure as shown in fig with the help of HCl and mercapto acetic acid.

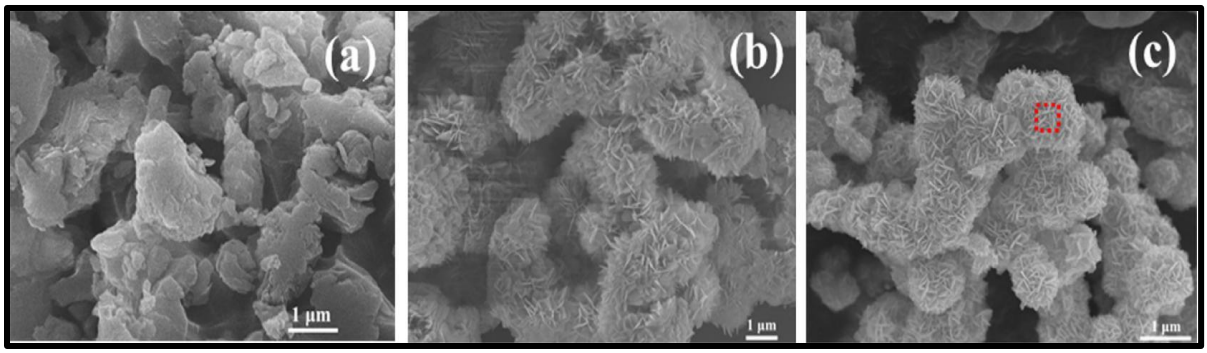


Fig.8 SEM images of g-C_3N_4 (a), SN (b), SN/CN (c and d)

Hao shen et al. [36] showed that the core shell structures of SnO_2@ g-C_3N_4 were prepared

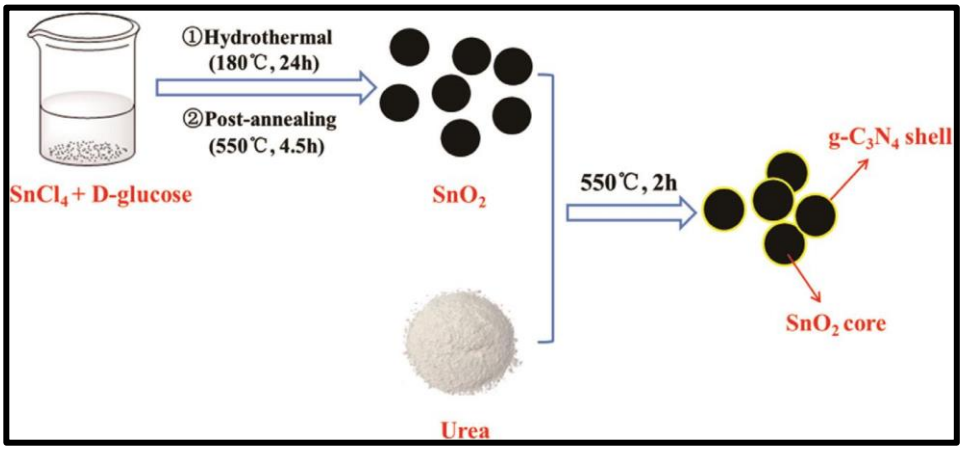


Fig 9 The preparation process of SnO_2@g-C_3N_4 core-shell structures.

with large interface contact area between the core of SnO_2 and core shell of g- C_3N_4. The as prepared core shell structure showed the enhanced photocatalytic activity than pure SnO_2 and g-C_3N_4 under visible irradiation on the basis of PL , XPS , EIS spectra.

CHAPTER 3 : Materials and Methdology

In the first chapter we deal with the research work ,some basic concepts, materials, instruments and the principles of the main analytical methods electron microscopy, X-ray analysis, Energy dispersive spectroscopy(EDS), UV-Visible Spectrophotometer and specific surface area measurement.

3.1 Apparatus Used

Test tubes (10 mL), Beakers (50 mL and 250 mL), Test tube stand, measuring cylinders, glass rod, filter papers, flask (50 mL), micro-pipette, magnetic beads, Petric plates ,crucible, spatula, dropper, pH paper, pH balance.

3.2 Reagents and Chemicals

All the chemicals were purchased from Aldrich. Stannous chloride precursor was used as a tin source. Ammonia solution was prepared to balance the pH. Rhodamine B was used to check the photocatalytic activity of catalyst under visible light.

3.3 Instruments Used

3.3.1 Weighing Balance

To measure the accurate quantities of chemicals a weighing balance (SARTORINS) is used.

Fig 10 Weighing balance

3.3.2 Sonicator

Fig 11 Sonicator

3.3.3Magnetic Stirrer

This device is used while preparing SnO_2.

Fig 12 Stirrer

3.3.4 Hot air oven

This device is used to dry the precipitates after the filteration proces.

Fig 13 Hot air oven

3.3.5 Laboratory Centifuge

To separate the two immiscible liquids centrifuge is used. Centrifugation is a process that involves use of centrifugal force for the sedimentation of heterogenous mixture.

Fig 14 Laboratory Centrifuge

3.3.6 Muffle Furnace

A muffle furnace is used in various labs to determine the proportion of samples which are non-volatile. It is used to calcine the samples. It can achieve a maximum temperature of 600^0C

Fig15 Muffle Furnace

3.4 Photochemical Reactor : This instrument is used for the dye degradation. This instrument needs no high voltage or neither water cooling. With fan the normal operating temperature is 35^oC and without fan it is approximately (60-70^oC). Ultraviolet light is 1.65*10 photons/sec/cm^3at 2537A.

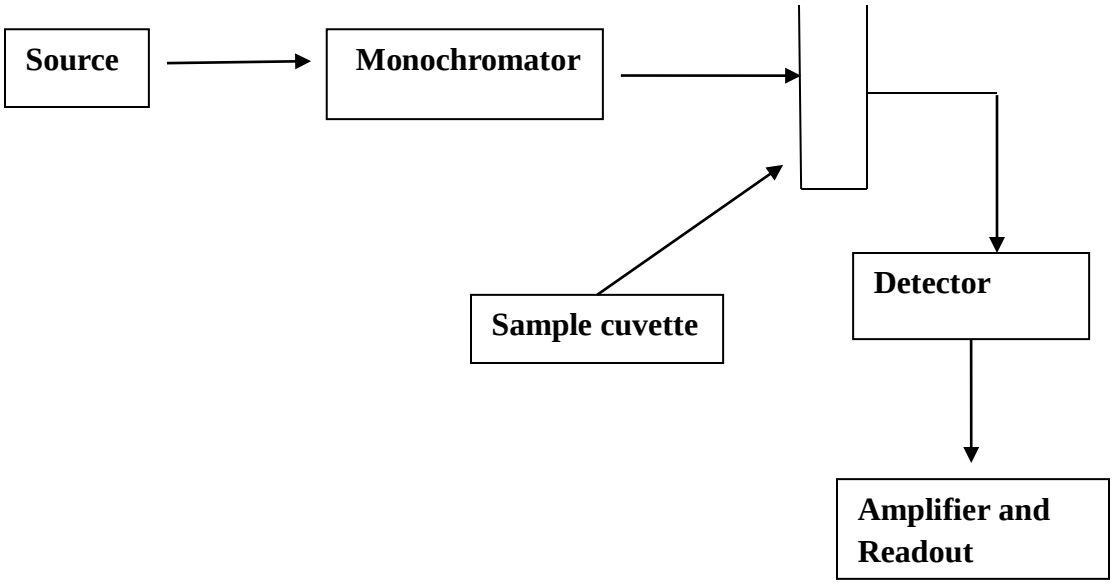
In this instrument the UV-lamp is cheap and has power consumption is 400 Watts and life time is near about 3000 hrs.

Fig 16 Photochemical Reactor

3.5 UV-Visible spectrophotometer

The observation of dye degradation was observed with the help of UV-Visible spectrophotomerter. It is basedon absorption spectroscopy and uses light near IR regions and near UV.This instrument is used for the chemical analysis, food safety analysis ,blood analysis, DNA/RNA conc. Analysis and residual chlorine analysis. It is based on the principle of Lambert-Beer's Law.

Fig 17 Block diagram of UV-Spectrophotometer



3.6 Transmission Electron Microscopy

TEM (Transmission electron microscopy) work on the similar as light microscope but in this case electrons are used rather than light. In TEM we get resolution thousand times greater than that of light microscope. In this instrument images are formed on the fluorescent screen by using transmitted beam or diffracted beam. In TEM there is electron gun for the production of electrons. To stop the large angle diffracted beam, magnetic lens is used. If there is any diffracted beam than aperture is used to eliminate this. Images are recorded on the fluorescent screen and we get 3D profile which are helpful for detecting the surface roughness.

3.7 BET Surface area analyzer

It is based on the principle of adsorption of gases on the surface. At a given pressure, the surface area is dependent on the amount of gas adsorbed. This is reliable and fast method for the determination of surface area. Monolayer is determined by Langmuir adsorption and multilayer is by BET theory.

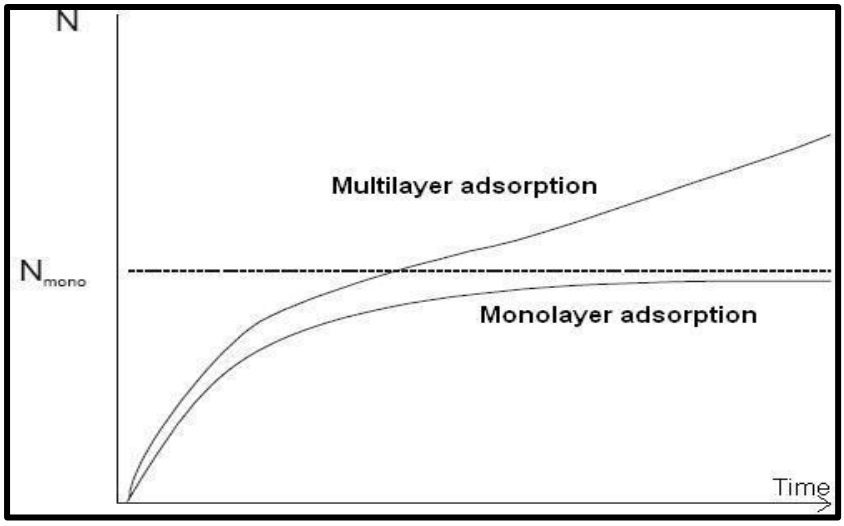


Fig-18 BET surface analyzer

In physical adsorption six types of isotherms are exist. Type I isothem is shown by microporous materials. Nonporous and macro-porous materials shown Type II and Type III respectively. Mesoporosity is shown by Type IV and Type V. Rarely used isotherm is Type VI. The isotherms arises because of the different types of interaction take place between the adsorbent and adsorbate. So microporous , macroporous and mesoporous materials show different behaviours.

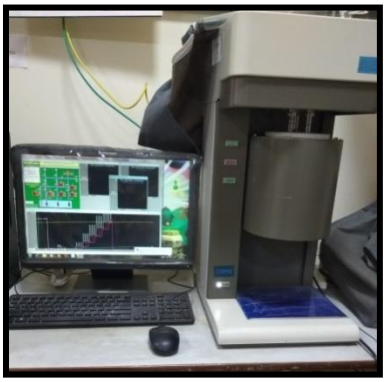


Fig 19 BET Instrument

Type III and Type V exhibit weak interactions between adsorbent and gas.

Types VI ,Types II and Types IV can be analyzed by BET method.

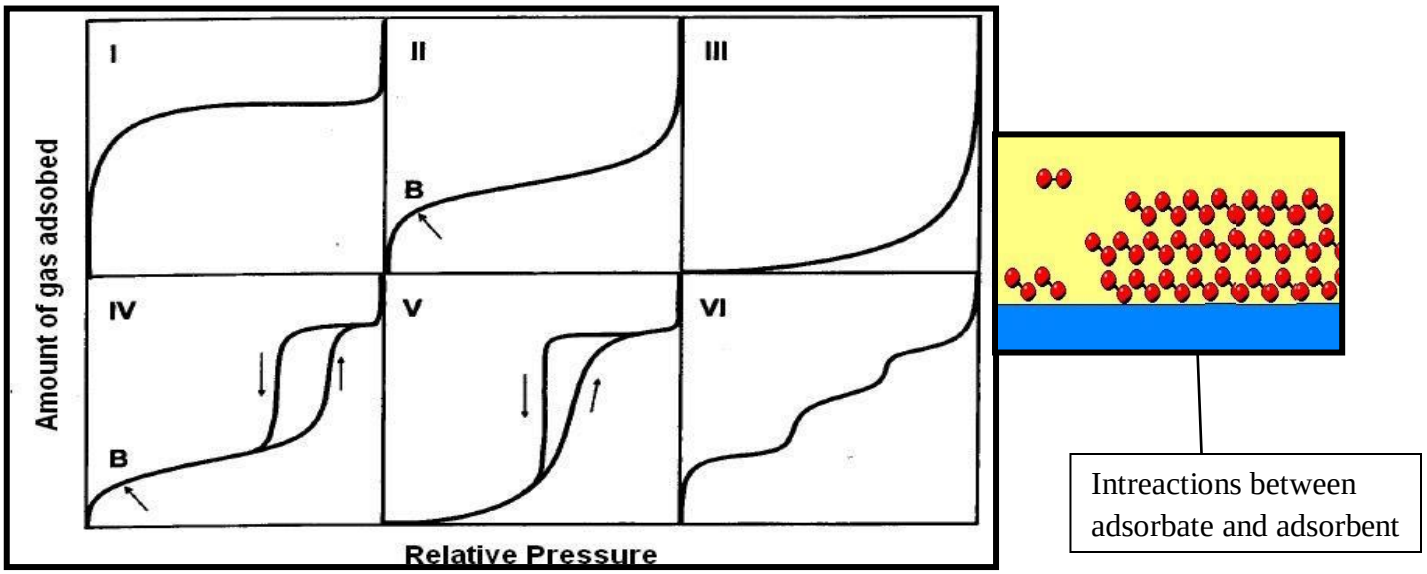


Fig20 Classification of gas adsorption isotherm

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3.8 Preparation of g-C_3N_4

- 12 gm of urea was taken and dissolved in 60 ml of water in crucible.
- Kept in hot air oven at 60Oc for 12 hours for its recrystallization.
- The recrystalyzed urea is kept in a muffle furnace at 550^0 C for 2h. Under nitrogen atmosphere.
- Light yellow colour is obtained which is g-C_3N_4.

3.8.1 Synthesis of SnO_2

- Prepare a 0.1 M solution of tin (IV) chloride by dissolving 0.876 g of SnCl4·5H2O in 25 ml distilled water.
- In this mixture 25% ammonia solution ($NH_3 \cdot H_2O$) was added drop-wise with constant stirring.
- Continued until the pH of the solution reached a value between 8 and 9.
- A white, cloudy solution was obtained, which is precipitated form of SnO_2.

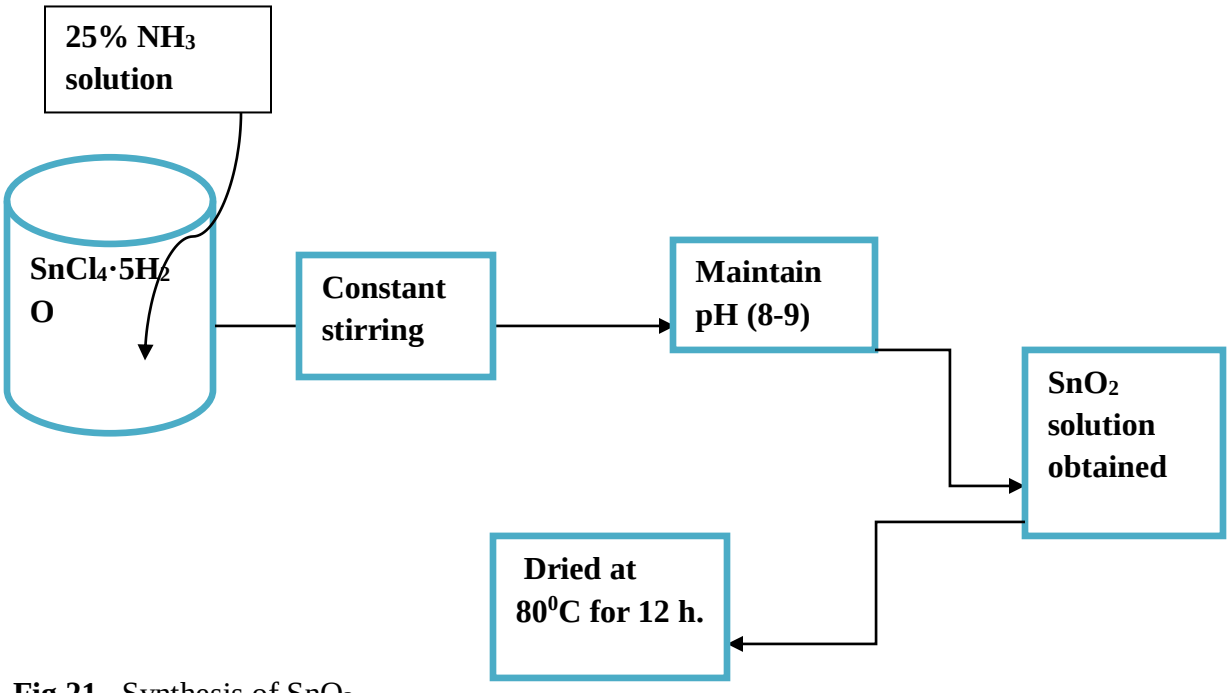


Fig 21 Synthesis of SnO_2

3.8.2 Fabrication of SnO_2/g-C_3N_4 composite photocatalyst

- In a typical synthesis, 50 mg of g-C_3N_4 was dispersed in 50 mL of water in a 250mL beaker for sonication for 2 h.
- SnO_2(50mg) was added to the solution and sonicate it for 2h .
- After that the mixture was stirred for 12 h.
- The white solid was separated by centrifugation, washed with water several times, and dried at 80^0C for 12 h.
- According to this method, a series of SnO_2/g-C_3N_4 composites with selected mass ratios of SnO_2 and g-C_3N_4 (1:1, 1:3, 1:5, 3:1, and 5:1) were prepared by changing the quantity of SnO_2 and g-C_3N_4.

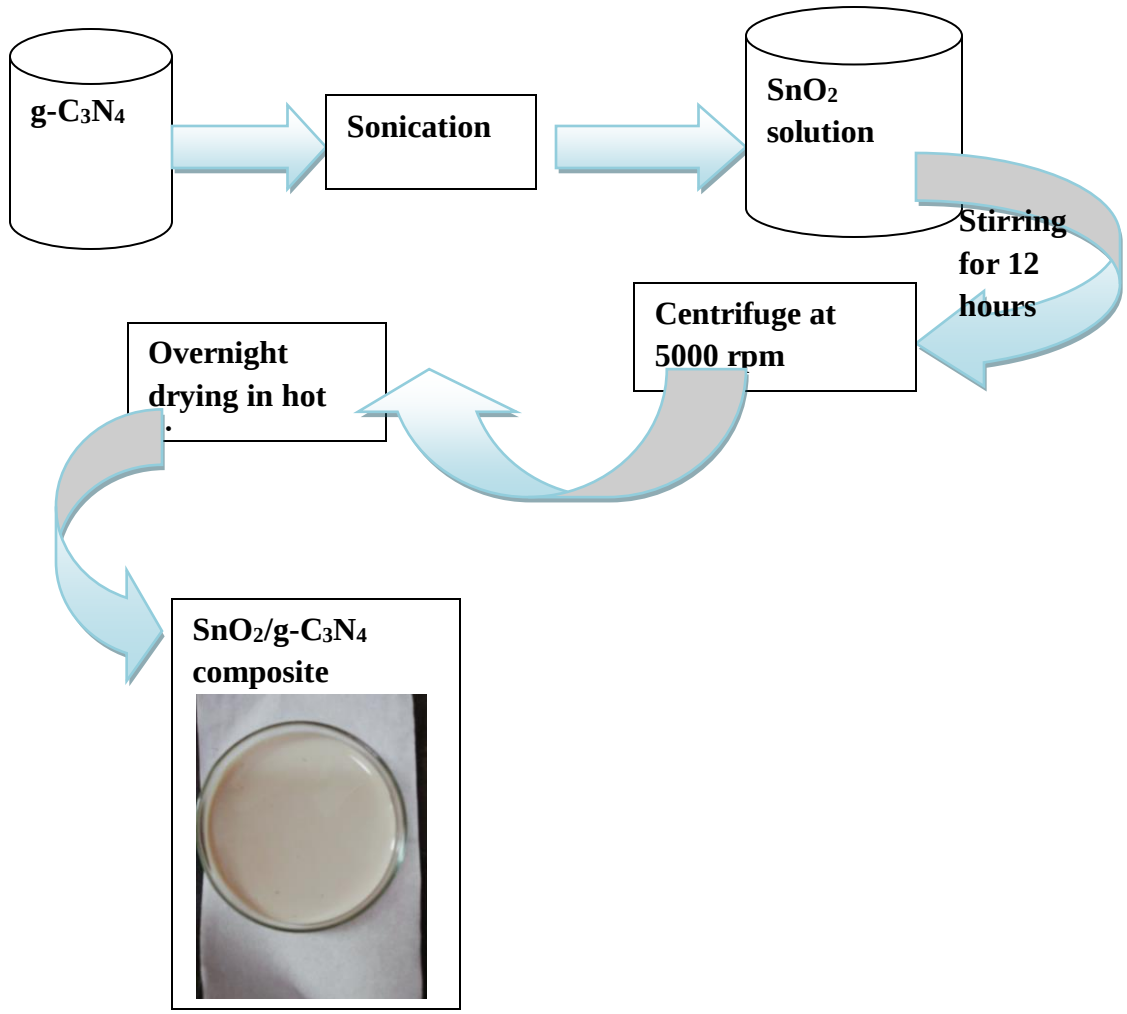


Fig22 Synthesis of nano-composite

3.8.3 Scheme for the Synthesis of nanocomposite SnO_2/C_3N_4.

A series of SnO_2/g-C_3N_4 composites with selected mass ratios of SnO_2 and g-C_3N_4 (1:1, 1:3, 1:5, 3:1, and 5:1) were prepared by changing the quantity of SnO_2 and g-C_3N_4.

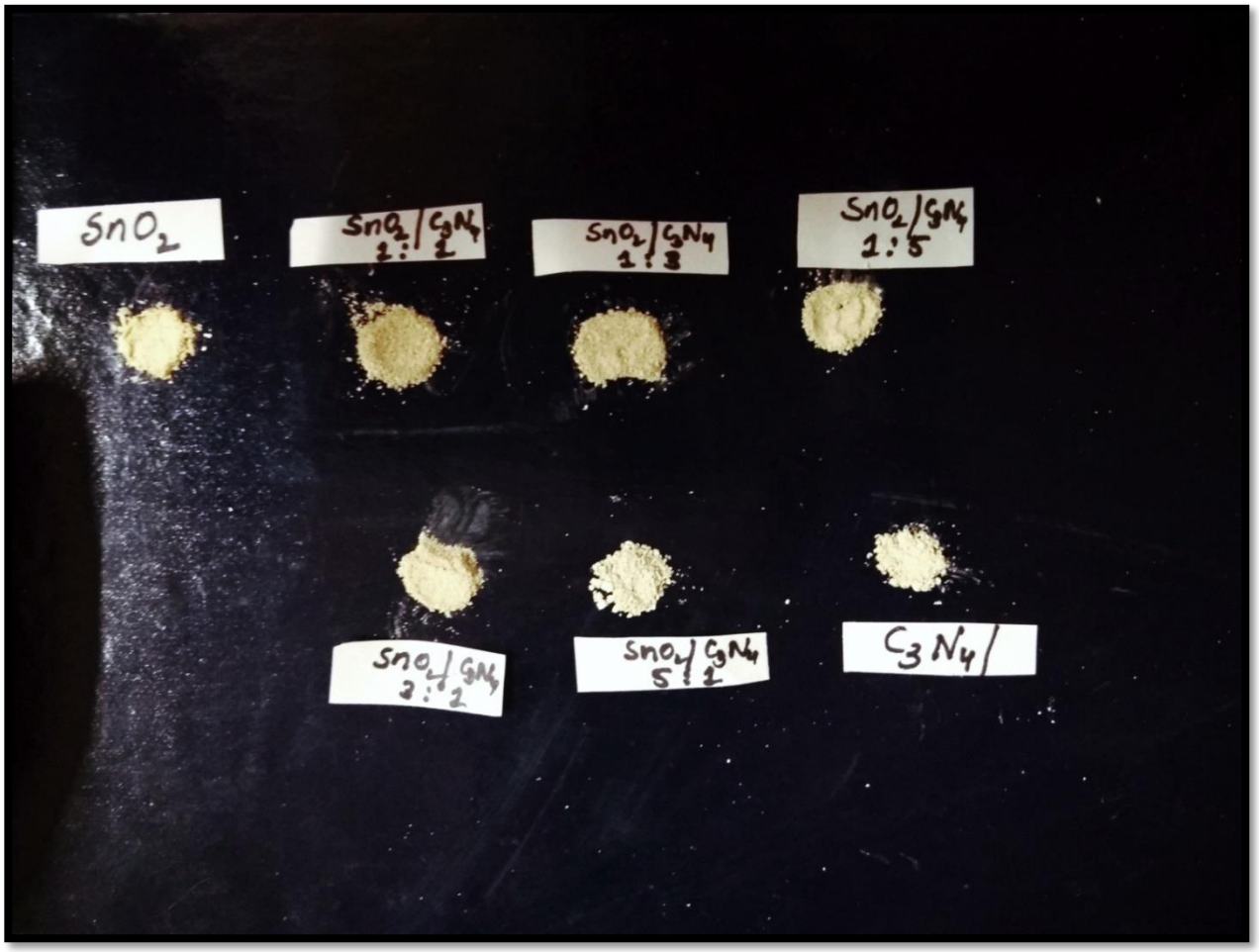


Fig23 Nanocomposite with different mass ratios**.**

3.9 PHOTOCATALYTIC ACTIVITY

3.9.1 Monitoring UV-visible spectra of Degradation of Rhodamine B using SnO_2/C_3N_4 catalyst

3.9.2 Chemicals required : Rhodamine B , deionised water, SnO_2 nanoparticles.

3.9.3 Procedure:

- Under visible light the photocatalytic performace of prepared catalyst were observed.
- Stock solution of dye was prepared by dissolving 20 mg of RhB in volumetric flask (1L) filled with distilled water.
- The glassware used during the reaction was doubled layered pyrex.
- To form suspension, the catalyst amount (2 mg) was dispersed in 5 mL of RhB solution.
- With continuous stirring at regular intervals of 10 min , 3 mL aliquots were pipette out with the help of micropipette and centrifuged.
- The maximum absorption peak of RhB was recorded by UV- Vis spectrophotometer (555nm)
- The degradation of RhB dye was calculated with the help of Lambert – Beer Law.

Fig24 Degradation of RhB using the nano-composite (SnO_2/C_3N_4)

Condition:- Oxygen was not bubbled during a photochemical reaction. Fig Degradation of RhB using the nano-composite (SnO_2/C_3N_4)

3.9.4 Determination of reactive species

In order to detect the active species generated in the reaction system, various representative scavengers, including methanol (5 mmol L^{1}, scavenger for OH), DMSO (C_2H_6OS, 5 mmol L^{1}, scavenger for h^+), and Ascorbic acid ($C_6H_8O_6$, 5 mmol L^{1}, e^-) were introduced into the solution before illumination.

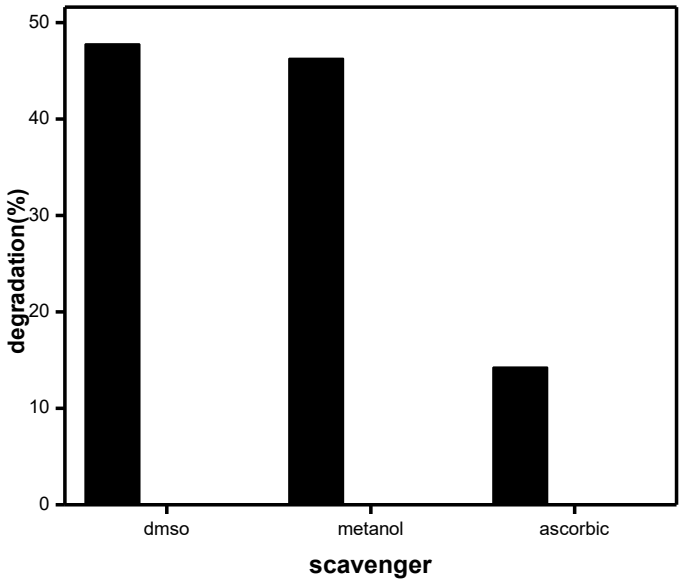


Fig 25 Degradation of RhB at different scavengers.

3.10 Degradation of Rhodamine B using SnO_2/C_3N_4 at different pH

RhB was degraded in the photochemical reactor with the help of nanocomposite SnO_2/C_3N_4 (1:1) at different pH values pH (1,3,5,7,9) and it was found that the maximum degradation was shown by the composite at pH = 7 that is at neutral conditions .

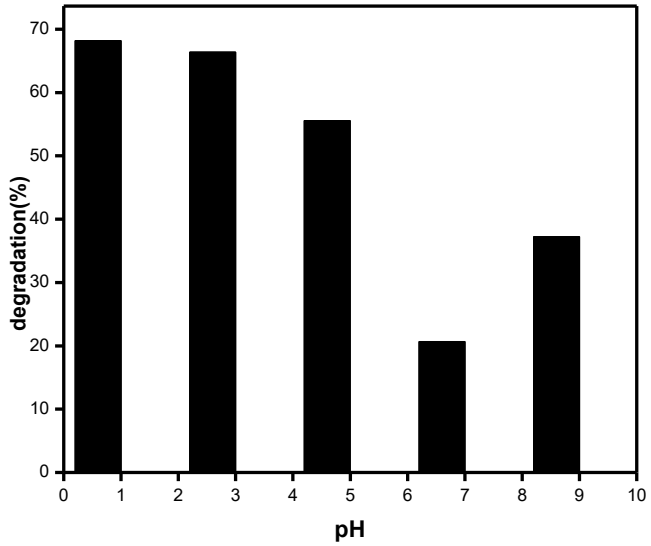


Fig26 Degradation of RhB at different pH values

3.10.1 Degradation of RhB using SnO_2/C_3N_4 by changing the catalyst amount

RhB was degraded in the photochemical reactor with the help of nanocomposite by changing the catalyst amount of SnO_2/C_3N_4 (2 mg, 4 mg, 6 mg, 8 mg, 10 mg) and it was found that the maximum degradation was shown by the catalyst at 2 mg as shown in the graph.

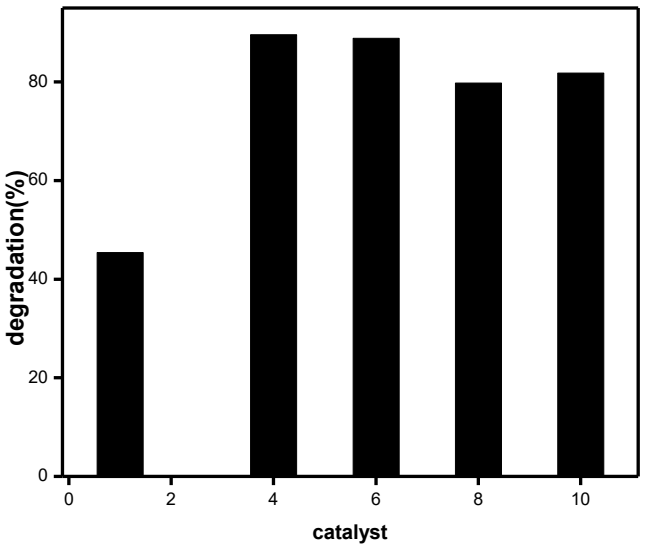


Fig 27 Degradation of RhB by changing the catalyst amount

CHAPTER: 4 Results and Discussion

4.1 Degradation of RhB dye with the help of nanocomposite under Visible light.

The degradation of RhB is carried out under the visible light at different time intervals using photocatalyst. The degradation was carried out to decrease the intensity of RhB solution treated with SnO_2/ C_3N_4 under UV-Visible light. In this way the composite with different mass ratios has been degraded with the help of RhB under visible light.

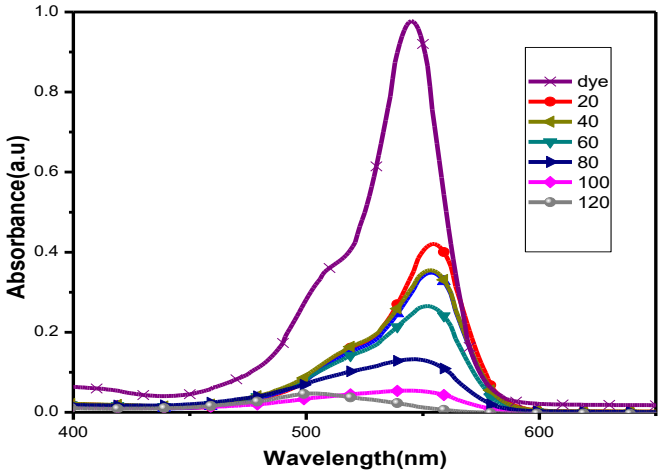
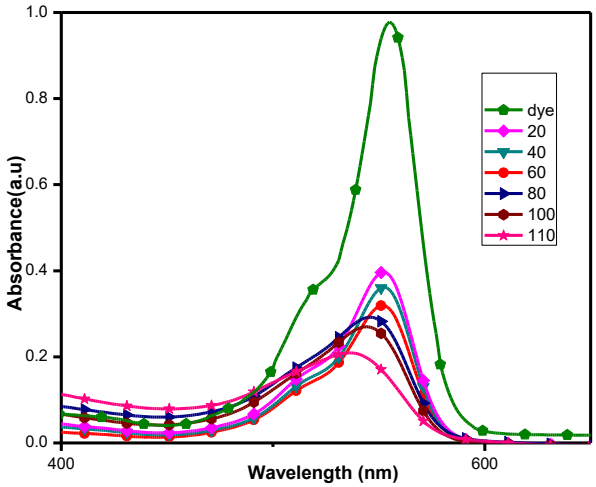


Fig28 Kinetic analysis of degradation of Rhodamine B using SnO_2/C_3N_4 (1:1) photocatalyst

This nanocomposite SnO_2/C_3N_4 (1:1) showed the 97% degradation of Rhodamine B under visible light in 120 min.

4.1.1 Photocatalytic activity of Nanocomposite :-SnO_2/C_3N_4 (3:1)



The nanocomposite as prepared showed 80% degradation under visible light in 110 minutes.

4.1.2 Photocatalytic activity of Nanocomposite :-SnO_2/C_3N_4 (5:1)

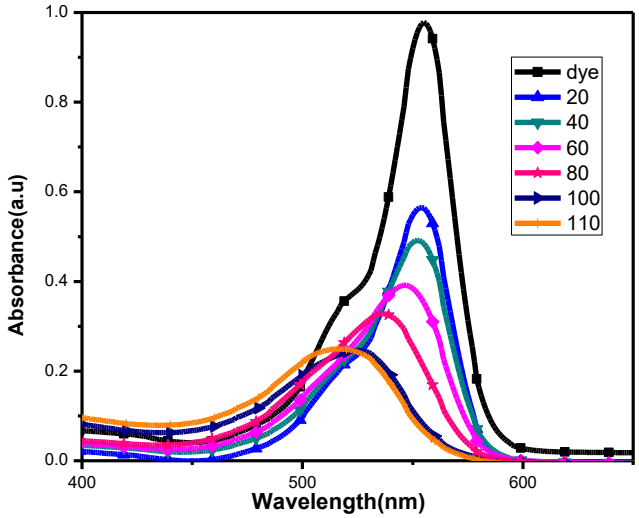


Fig29 Kinetic analysis of degradation of RhB using SnO_2/C_3N_4 (5:1)

This nanocomposite SnO_2/C_3N_4 (5:1) showed the 77% degradation of Rhodamine B under visible light.

4.1.3 Photocatalytic activity of Nanocomposite :-SnO_2/C_3N_4 (1:3)

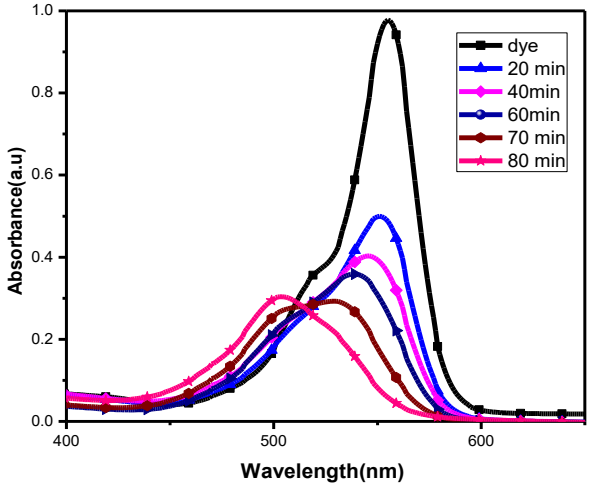


Fig30 Kinetic analysis of degradation of Rhodamine B using SnO_2/C_3N_4

This nanocomposite SnO_2/C_3N_4 (1:3) showed the 84% degradation of Rhodamine B under visible light.

4.1.4 Photocatalytic activity of Nanocomposite :-SnO_2/C_3N_4 (1:5)

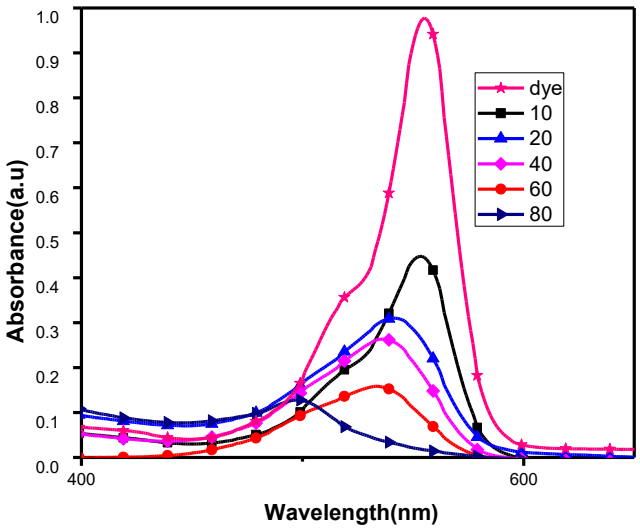


Fig 31 Kinetic analysis of degradation of Rhodamine B using SnO_2/C_3N_4 (1:5)

This nanocomposite SnO_2/C_3N_4 (1:5) showed the 92% degradation of Rhodamine B under visible light.

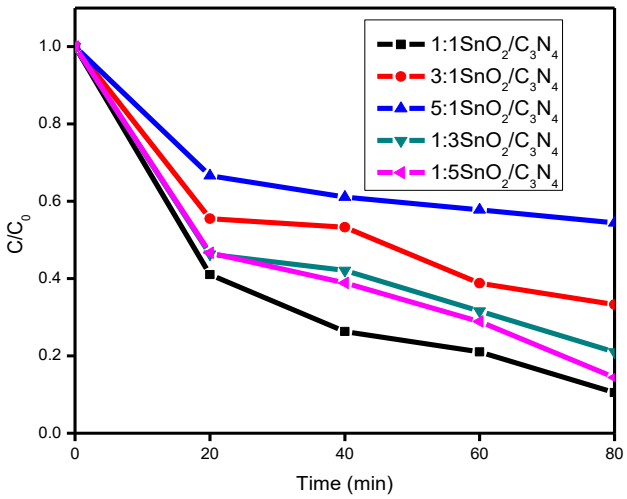


Fig 32 Degradation of RhB in the presence of SnO_2/C_3N_4 photocatalyst using different mass ratios.

4.2 XRD Diffracation pattern

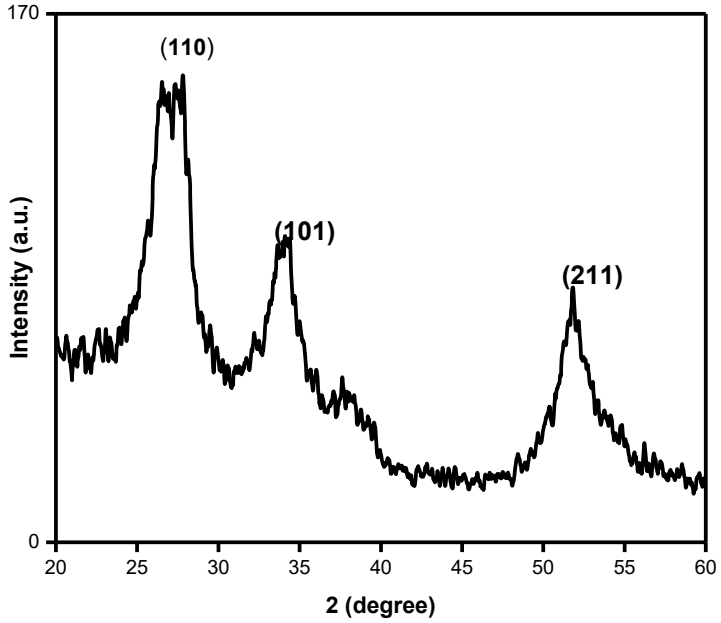


Fig 33 XRD pattern of nanocomposite SnO_2/C_3N_4(1:1)

The peaks at 2θdegree values of 26.3^0, 34.0^0 and 51.9^0 are associated with (110), (101) and (211) planes respectively. The total peaks can be record as clear crystalline rutile stannic oxide (JCPDS 1147). In XRD pattern there is broaden-ing of (110) peak which shows that there is existence of nanocomposite SnO_2/C_3N_4(1:1) and also there is no impurities such as Sn_2S_3 and SnO.

4.3 XPS(X-ray photoelectron spectroscopy technique)

The valence performance of prepared nano-composite SnO_2/g-C_3N_4 is characterized by XPS . Fig. 34 showed the spectra of pure g-C_3N_4, SnO_2 and SnO_2/C_3N_4 with different mass ratio. These results clearly showed that O, N, C, Sn co-exist in the nanocomposite. The spectra of O 1s, C 1s, N 1s and Sn 3d are shown below. The nanocomposite g-C_3N_4/SnO_2 (1:1) photocatalyst , binding energies of $Sn_{5/2}$and $Sn_{3/2}$ have 496.20 eV and 488.20eV values respectively. The phenomenon is because of intimate interactions among Sn^{4+} and g-C_3N_4.

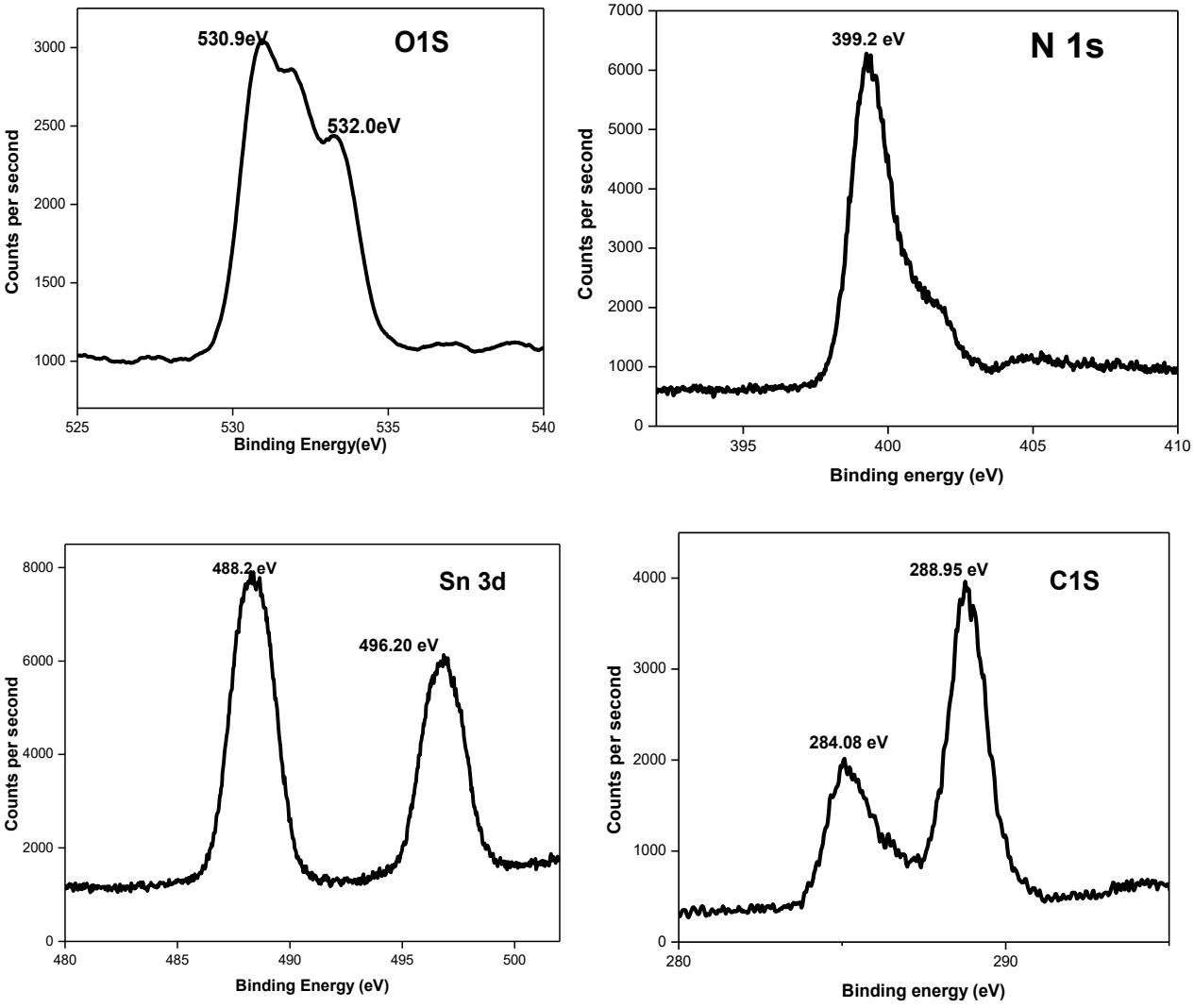


Fig 34 XPS spectrum of a) O1S b) N1S c) Sn 3d d) C1S

4.4 Energy Dispersive analysis (EDS)

The EDS (Energy Dispersive analysis) confirms the elemental information of the catalyst According to this image the presence of tin, nitrogen, oxygen and carbon can be inferred. This spectra revealed that the there is uniform deposition of SnO_2 nanoparticles on the surface of g-C_3N_4.

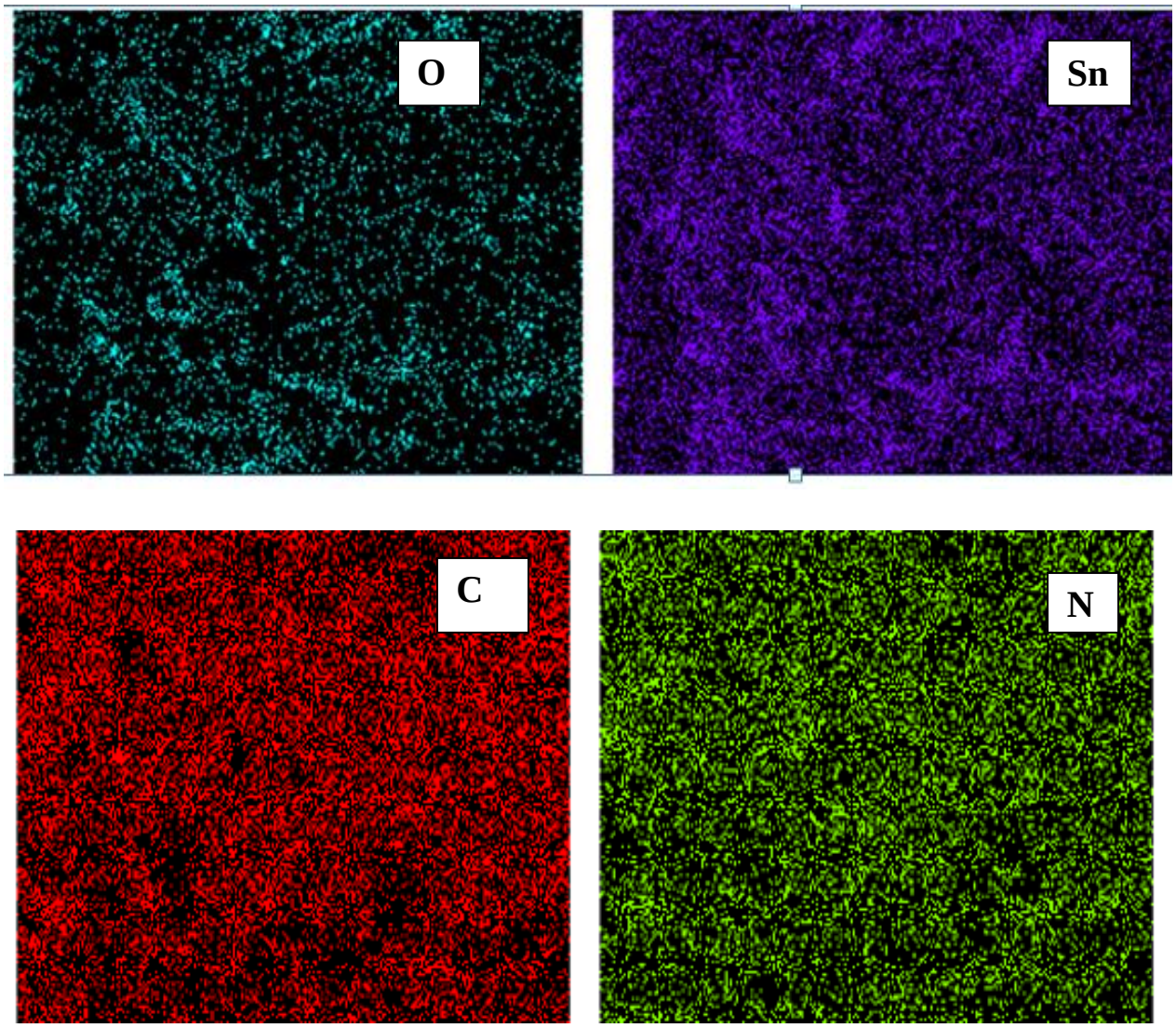


Fig 35 EDS spectrum of SnO2/C_3N_4 nanocomposite

The weight % and atomic % of N , O , Sn, and C are given below

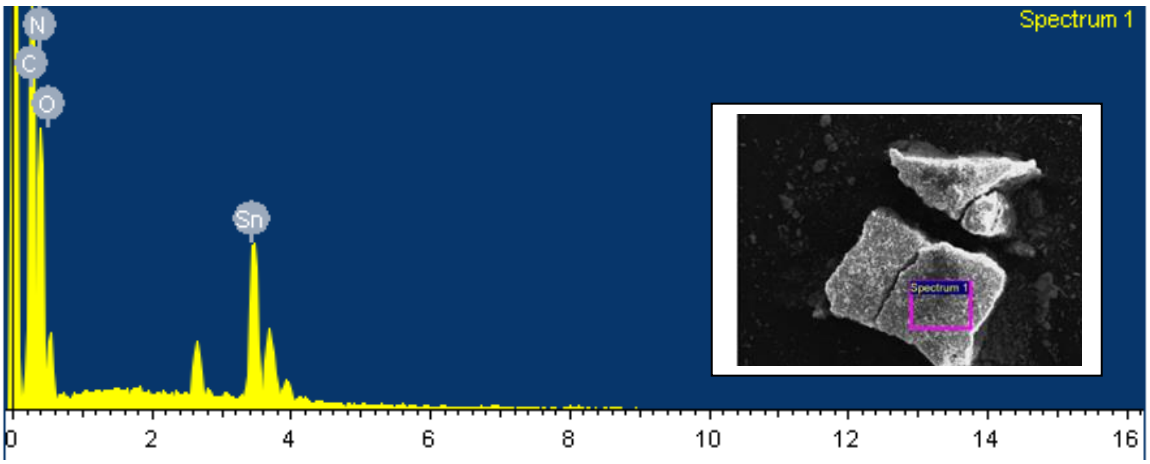


Fig36 Showed the Atomic % and weight % nanocomposite

Elements	Weight %	Atomic %
C K	22.40	32.13
N K	39.54	48.62
O K	14.74	15.87
Sn L	23.32	3.38
Total	100.00	

Table 1 Represent the weight and atomic percentage of prepared nanocomposite.

4.5Transmission Electron Microscopy

TEM image Fig (37) gives us a information about the two components. The light part confirm the presence of g-C_3N_4 and dark part confirm the spherical shape of SnO_2.which shows the dispersion of SnO_2 on the surface of g-C_3N_4. The high resolution transmission electron microscopy showed the microstructure of nanocomposite (g-C_3N_4/SnO_2). The spacing of interplanes are 0.2740 and 0.3476 which are very near to (101) and (110) planes of SnO_2 in according with XRD results. In the prepared nanocomposite their may be some close interface which is favourable for the charge migration between the g-C_3N_4/SnO_2 and leads to the e^- hole pairs. HRTEM images of the composite clearly showed that the hybrid present in structureare heterogeneous.

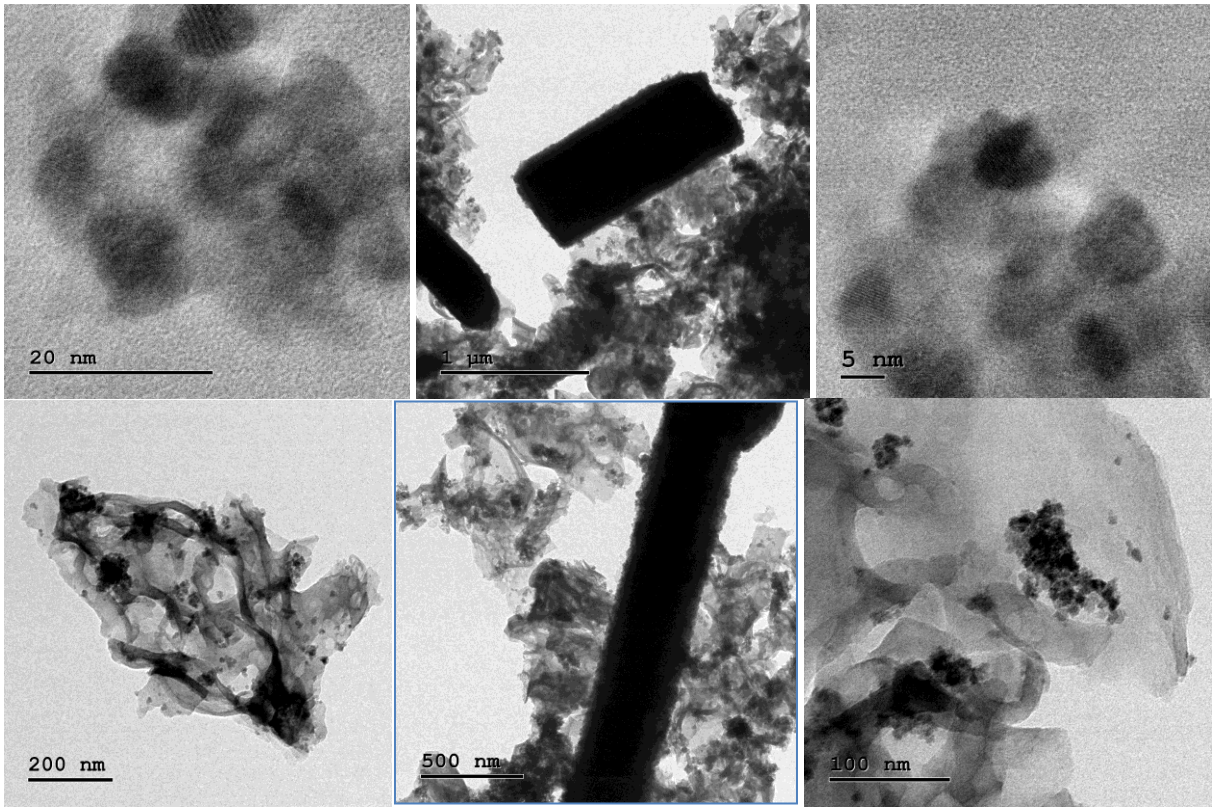


Fig 37 TEM images of SnO_2/ g-C_3N_4

4.6 Nitrogen Sorption Analysis (BET)

Table -4 represent the N_2 desorption/ adsorption isotherms for SnO_2/C_3N_4 catalyst with different mass ratio which showed their structural character. The nano-composite showed the adsorption isotherm type-IV with hysteresis loop which represent the uniformly distribution of pores. The highest surface area and the photodegradation was shown by $SnO_2/g\text{-}C_3N_4$(1:1) nano-composite.

Table 2: Summary of BET analysis of prepared catalysts.

Sample name	**Surface area**	**Total pore volume (cm^3)**	**Mean pore diameter(nm)**
SnO_2	32.5	0.139	17.17
$SnO_2/g\text{-}C_3N_4$ (1:1)	100.2	0.082	3.241
$SnO_2/g\text{-}C_3N_4$ (1:3)	59.8	0.1712	12.50
$SnO_2/g\text{-}C_3N_4$ (1:5)	70.5	0.1354	7.690
$SnO_2/g\text{-}C_3N_4$ (3:1)	49.6	0.315	25.44
$SnO_2/g\text{-}C_3N_4$ (5:1)	48.1	0.278	23.14

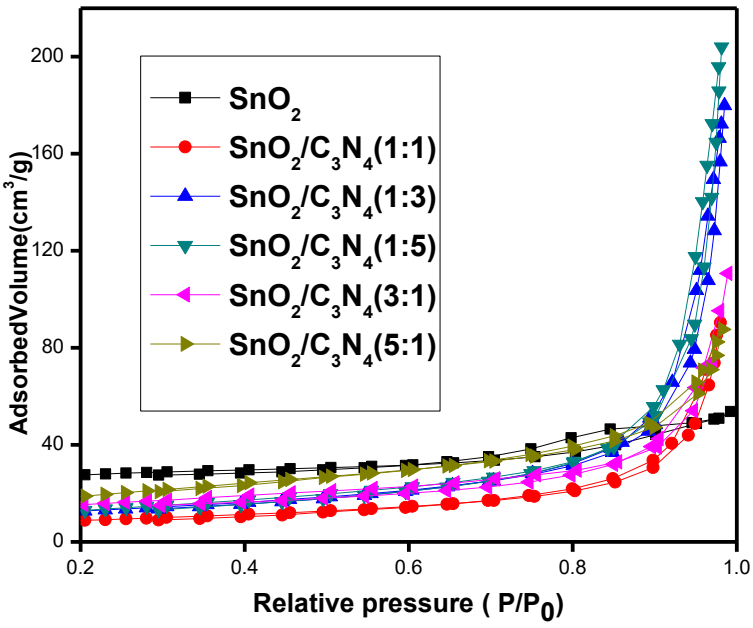


Fig 38 BET curves of the various heterogenous samples with different SnO_2/C_3N_4

4.7 Scanning Electron Microscopy

SEM is a electron microscopy by scanning the surface of sample with beam of electrons produces the images. SEM gives the information about crystalline structure, chemical composition and texture . The particle size of sample is found to be 400 nm shape is nano-rods.

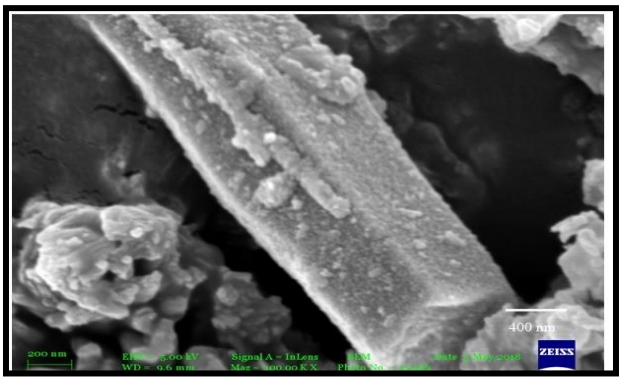


Fig 39 SEM image of SnO_2/C_3N_4

Chapter 5

Conclusion

SnO_2/C_3N_4 composite prepared by simple method using $SnCl_2.5H_2O$ precursor. The series of SnO_2/g-C_3N_4 composites with selected mass ratios of SnO_2 and g-C_3N_4 (1:1, 1:3, 1:5, 3:1, and 5:1) were prepared by changing the quantity of SnO_2 and g-C_3N_4. The photocatalytic activityof the prepared sample were evaluated by degradation of RhB using amount of catalyst 2 mg in 5 mL dye. The nano-composite SnO_2/g-C_3N_4 (1:1) showed the highest photocatalytic activity under visible light. The shape and structure of nano-composite was found to be nano rods and mesoporous respectively. From BET result it was found that SnO_2 was uniformly distributed on nano-meter scale and particle size was found to be 400 nm. The improved The higher photo-catalytic activity of SnO_2/g-C_3N_4 (1:1) could be due to the improved efficiency of charge separation and the large surface area.

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