

Synthesis Of Graphitic Carbon Nitride Composite With Zinc Oxide: Characterization And Evaluation Of Photo Catalytic Activities

Susmita Boruah, Nabajyoti Dutta

Abstract: In this present work, we have synthesized graphitic carbon nitride, zinc oxide, and zinc oxide composite with carbon nitride $g-C_3N_4/ZnO$. Methyl orange which is an azo-dye is used as a standard organic pollutant to observe the photo catalytic activity of $g-C_3N_4/ZnO$ and the degradation of this dye was studied. It was observed that the photo catalytic efficiency of $g-C_3N_4$ was increased when composites were prepared. In this present work, we have synthesized graphitic carbon nitrite, zinc oxide and zinc oxide composite with carbon nitride $g-C_3N_4/ZnO$. Methyl orange which is an azo-dye is used as a standard organic pollutant to observe the photo catalytic activity of $g-C_3N_4/ZnO$ and the degradation of this dye were studied. It was observed that photo catalytic efficiency of $g-C_3N_4$ was increased when composites were prepared.

Keywords: Composite, photo catalyst, dye degradation, Methyl orange.

1 INTRODUCTION

From the last few years, photo catalytic techniques have been widely used to treat waste water. Because it helps in the quick oxidation of most of the organic compound, no formation of carcinogenic polycyclic product and it also helps in the oxidation of organic pollutants up to the parts per billion (ppb) levels. Methyl orange which is an azo-dye can be used in textiles industry, leather and paper industry. Through it has wide use it can create a lots of pollution. Hence methyl orange is chosen to study the dye degradation process [1]. $g-C_3N_4$ is a polymeric compound which is the allotrope of carbon[2] having optical band gap 2.7 eV. $g-C_3N_4$ has great attention in the degradation of pollutants because it has high sensitivity as a photo catalyst[3]. But there is a limitation in the use of this $g-C_3N_4$ because it has high recombination rate of the photo generated electron-hole pairs and due to this fluorescence yield and it leads to the decrease in the photo catalytic activity of the $g-C_3N_4$. Hence to overcome this problem we have to

suppress the recombination rate of e^- and hole which can be generated by using light radiation of suitable frequency. We have to use two semiconductor having suitable matching in the valence and conduction band which offers a suitable driving force to separate and transfer photo generated hole pairs. In the present work e^- and h^+ is try to generate by irradiation in $g-C_3N_4$ using visible-light. e^- is generated in $g-C_3N_4$ and this e^- transformed to ZnO (Semiconductor) while the photo

generated holes stay in the $g-C_3N_4$. Thus separation of e^- and hole takes place and it suppress the recombination of e^- and hole and it helps to improve the photo catalytic activity. The e^- which is now present in ZnO combine with O_2 and form O_2^- and the following reactions takes place and leads to the degradation of the dye methyl orange.

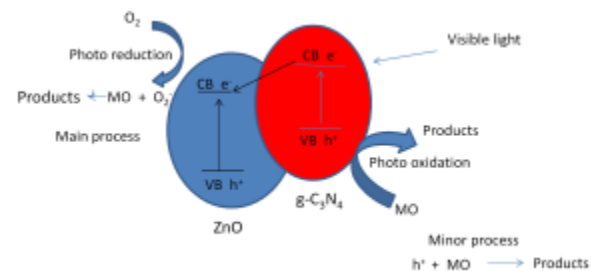
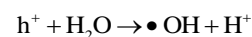
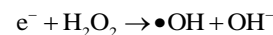
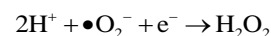
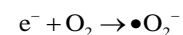


Fig1: Schematic illustration of electron-hole separation under visible light irradiation.



2 REVIEW OF LITERATURE

Nasr et al; reported that dyestuffs and some other commercial colorants create lots of pollution by releasing toxic, carcinogenic substances in water. So, they studied the different method for the removal of these pollutants [4]. More et al. and Patil et al; used the conventional technologies to degrade the dye. The techniques used by them are non

- Susmita Boruah, M.Sc. in Chemistry, Dibrugarh University. E-mail: susmitaboruah2015@gmail.com
- Nabajyoti Dutta, Ph.D. Research Scholar, Dibrugarh University. E-mail: njduttamaths2013@gmail.com

destructive because this techniques helps to degrade the non-biodegradable substances into degradable one or to the harmless product [5-6]. Brown and Darwent reported that organic dye such as methyl orange present in water can be degraded by using colloidal TiO_2 . They reported that in absence of TiO_2 this degradation will-not occur. The

generation of e^- hole pairs in the semiconductor helps in the degradation of this type of dye [7-9]. Fujishima et al. also studied the decomposition of organic compound in water in combination with TiO_2 [10]. Daheshvar et. al use ZnO as a photo catalyst in the degradation of azo dye [11]. Chen et. al uses solvothermal method to synthesize Ag/ZnO nano catalyst. To characterize this they use X-ray (XRD) and TM. They uses Ag/ZnO to degrade MO. They reported that the dye MO is degraded within 60 min [12]. Roselin et al., reported the photo degradation of Reactive Red 22 (RR22) dye in presence of ZnO photo catalyst at different interval of time.

They also examined the effect of p^{H} , amount of ZnO coating etc [13]. Chakrabarti et al examined the photo degradation of methylene blue and Eosin Y in the presence of ZnO semiconductors. They also investigated the effect of loading of catalyst, air flow rate, intensity of used UV radiation, and p^{H} during the degradation process [14]. Wang et. al first reported the metal free photo catalytic degradation of organic pollutants by using $\text{g}-\text{C}_3\text{N}_4$ [15]. Yan et al. also successfully reported that $\text{g}-\text{C}_3\text{N}_4$ can be used in the photo degradation of organic pollutants. They investigated that photo catalytic property of $\text{g}-\text{C}_3\text{N}_4$ can be increased by using Ag as a co-catalyst. They prepared $\text{g}-\text{C}_3\text{N}_4$ by using melamine [16]. Sun at al. prepared $\text{g}-\text{C}_3\text{N}_4$ composite with ZnO by simple calcinations method. From their observation they get the information that $\text{g}-\text{C}_3\text{N}_4-\text{ZnO}$ composite has greater degradation power [17]. Yuan et. al reported the synthesis of $\text{g}-\text{C}_3\text{N}_4$ nano sheets/ ZnO through facile precipitation calcinations. They use it to reduce aqueous Cr(VI) under visible light [18].

3. EXPERIMENTAL METHODS AND MATERIALS SECTION:

Here we are describing the experimental procedures involved in synthesis of ZnO and $\text{g}-\text{C}_3\text{N}_4$, $\text{g}-\text{C}_3\text{N}_4$ composite with ZnO and the materials and apparatus used.

3.1 Materials:

The chemicals used in the process were urea, Zinc nitrate hexahydrate, Zinc acetate, Sodium hydroxide and hexamine.

3.2 Synthesis of $\text{g}-\text{C}_3\text{N}_4$:

The polymeric $\text{g}-\text{C}_3\text{N}_4$ sheets were synthesized by thermal polydegradation of urea followed by decomposition. Here, 2 g of urea was taken in a mortar pestle and it was ground for about 15 minutes. This ground urea was put into a silica crucible with a cover and placed in a muffle furnace for 1 hour at 450°C . After cooling the furnace to room temperature the product was taken.

3.3 Synthesis of ZnO(N) :

For the synthesis of ZnO(N) , 5 mmol of Zinc nitrate hexahydrate (1.485 g) was dissolved in 25 ml of water with constant stirring. An equimolar amount of NaOH (0.2 g was dissolved in water) was added to the reaction mixture drop wisely. Then filtered the precipitate and dried the precipitate at 100°C for overnight.

3.4 Synthesis of ZnO(H) :

For the synthesis of ZnO(H) , 5 mmol of Zinc nitrate hexahydrate (1.485 g) was dissolved in 25 mL of water with constant stirring. 0.5 mmol of Hexamine in 25 mL of H_2O was added drop wisely to the reaction mixture and placed the mixture in a oven for 5 hours, then sonicated this and filtered the ppt and dried it at 100°C for overnight.

3.5 Synthesis of ZnO(C) :

For the synthesis of ZnO(C) , 4 g of Zinc acetate was taken in a silica crucible and placed it in a muffle furnace for 1 hour at 450°C .

3.6 Synthesis of $\text{g}-\text{C}_3\text{N}_4-\text{ZnO}$ (Insitu), $\text{g}-\text{C}_3\text{N}_4-\text{ZnO(C)}$, $\text{g}-\text{C}_3\text{N}_4-\text{ZnO(H)}$, $\text{g}-\text{C}_3\text{N}_4-\text{ZnO(N)}$ composite:

The $\text{g}-\text{C}_3\text{N}_4-\text{ZnO}$ (Insitu), is prepared by taking 3.570 g of Zinc acetate and 0.05970 g of urea in mortar and then grind it and taken into a silica crucible and placed the crucible in muffle furnace for 1 hour at 450°C . Then we get $\text{g}-\text{C}_3\text{N}_4-\text{ZnO}$ (In situ) (.02:1). The another composite $\text{g}-\text{C}_3\text{N}_4-\text{ZnO(C)}$ was prepared by simply adding 1 g of ZnO (obtained by heating Zinc acetate at 450°C for 1 hour) and 20 mg of $\text{g}-\text{C}_3\text{N}_4$ and then grind it. we get $\text{g}-\text{C}_3\text{N}_4$ composite with ZnO(C) .

Similarly, $\text{g}-\text{C}_3\text{N}_4-\text{ZnO(H)}$, $\text{g}-\text{C}_3\text{N}_4-\text{ZnO}_2(\text{N})$ composites were prepared.

3.7 Measurement and Material characterization:

The crystalline structure of the prepared $\text{g}-\text{C}_3\text{N}_4$, ZnO and $\text{g}-\text{C}_3\text{N}_4$ composite with ZnO were determined by powder X-ray diffraction (PXRD). To analyse this sample a Bruker D2 PHASER X-ray diffractometer with (Cu-K) X-ray generator was used. The operating voltage of this is 30 KV and current used here is 10 mA. To record the PXRD pattern in a wide range of 2θ (i.e. $5-80^\circ$) fixed scan rate was used which is 0.1°s^{-1} . To investigate the absorption of materials and dye degradation JASCO model V-650 spectrophotometer was used. It provided the diffuse reflectance UV-Vis spectra (DRS). This spectrophotometer has a 150 mm integrating sphere and BaSO_4 is used as internal standard. To carried out the steady state photoluminescence (PH) measurements Horiba-JobinYvon Fluoromax 4C spectrophotometer was used.

4. RESULTS AND DISCUSSION:

4.1 PXRD analysis:

PXRD is used for phase identification of prepared $g-C_3N_4$, ZnO and $g-C_3N_4$ composite with ZnO. This was done by scanning the different samples through a range of 2θ angles. In the fig 2 an intense peak is observed at $2\theta = 27.65$ due to the conjugated system of aromatic ring having 002 crystal face and interlayer distance (d) = .32nm. Another intense peak is observed at $2\theta = 12.90$ having interlayer distance of 0.680 nm and 001 crystal face is due to tri-s-triazine unit.

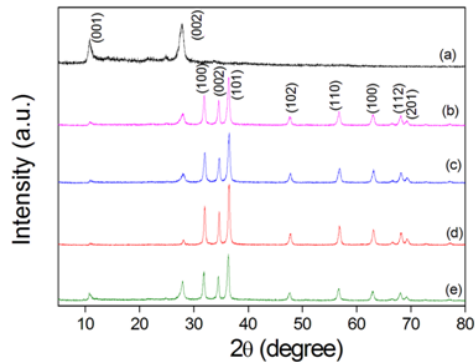


Fig. 2: XRD patterns of the synthesized (a) $g-C_3N_4$, (b) $g-C_3N_4-ZnO$ (N), (c) $g-C_3N_4-ZnO$ (C), (d) $g-C_3N_4-ZnO$ (H), (e) $g-C_3N_4-ZnO$ (Insitu).

XRD pattern of the prepared composite are also presented in the fig 2. Trace (b), (c), (d), (e) represent the PXRD pattern of the composites. The peak at $2\theta = 12.90$ and $2\theta = 27.65$ indicates the presence of $g-C_3N_4$ in the prepared composite samples. The diffraction peaks at 31.80° , 34.11° , 36.93° , 47.8° , 56.91° , 62.11° , 68.13° , and 69.18° have been keenly indexed as hexagonal wurtzite structure of ZnO with lattice parameters $a = b = 0.32$ nm, $c = 0.52$ nm. These lattice parameters are quite similar to Suresh and Sandhu[19] who reported lattice parameters $a = b = 0.323$ nm, $c = 0.52$ nm for wurtzite geometry of ZnO [20].

4.2 Diffuse reflectance UV-visible absorption analysis of various $g-C_3N_4-ZnO$ composite:

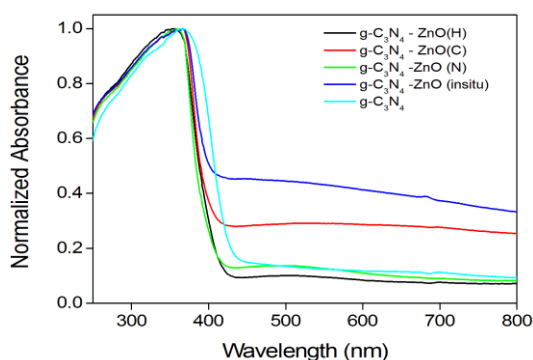


Fig. 3: DR-UV-vis spectra of $g-C_3N_4$ and various $g-C_3N_4-ZnO$ composites.

A sharp absorption at 450 nm due to $g-C_3N_4$ which exhibits a band gap of 2.88 eV. The absorption wavelength of $g-C_3N_4-ZnO$ extended towards the visible region. Absorption intensity is also increased which clearly indicates the effective surface coupling of ZnO with $g-C_3N_4$. And we can expect that this will help to increase the photo catalytic activity of the composite.

4.3 Steady state Photoluminescence (PL) spectra analysis:

Transfer of e^- , generation of hole (h^+) and recombination rate of e^- and h^+ were studied through PL analysis (fig 4). The excitation peak around 325 nm is due to N=C group present in 1,3,5-triazine unit. The peak at 340 nm may be due to the presence of terminal N-C group in $g-C_3N_4$. In order to study the effect of addition of ZnO to $g-C_3N_4$, the different composition were excited at wavelength 330 nm and 340 nm. In the figure (4) a strong peak at 440 nm is observed due to $g-C_3N_4$ and it is absent in the composites due to the low content of $g-C_3N_4$ in the composites. A peak at 410 nm is seen due to ZnO. PL peak intensity at 410 nm is different or different composites. PL peak intensity is lowest for $g-C_3N_4-ZnO$ (N). This indicates that this photo catalyst can efficiently suppress the recombination of e^- and h^+ . Hence it increases the photo degradation efficiency.

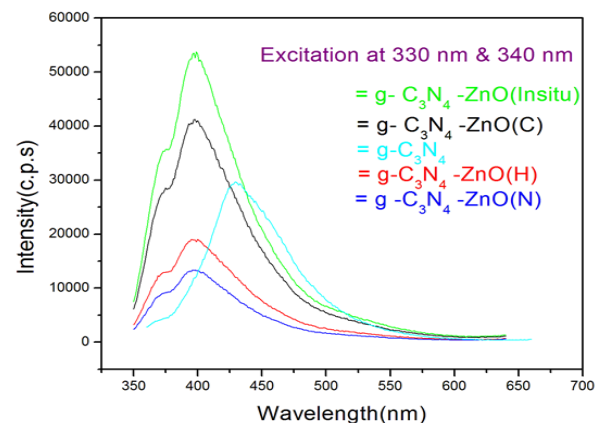


Fig 4: Emission spectra of $g-C_3N_4$ and various $g-C_3N_4-ZnO$ composites.

4.4 IR analysis:

As shown in figure 5 the $g-C_3N_4$ shows several peaks due to the vibrations of some bonding occurs between carbon and nitrogen

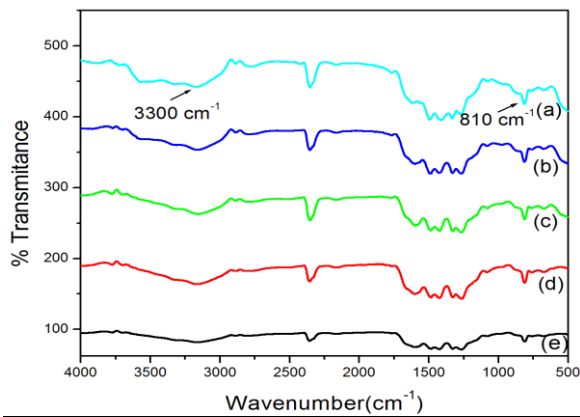


Fig. 5: IR spectra of (a) $g-C_3N_4$, (b) $g-C_3N_4-ZnO(C)$, (c) $g-C_3N_4-ZnO$ (In situ), (d) $g-C_3N_4-ZnO(H)$, (e) $g-C_3N_4-ZnO(N)$

The absorption peak at 810 cm^{-1} is due to the triazine unit of $g-C_3N_4$. The absorption peak at $3100-3300\text{ cm}^{-1}$ is due to primary and secondary amines with intermolecular hydrogen bonding [21]. Peaks at $1200-1600\text{ cm}^{-1}$ are due to stretching vibrations of C-N hetero-cycles. The entire observed peaks in $g-C_3N_4$ are similar to the reported previously. The peak at 1600.92 cm^{-1} is due to stretching vibration of conjugated C-N (carbon nitride). The absorption peak at 1483.26 cm^{-1} is related to the ring stretching vibrations of conjugated C=N. Again absorption at 1328.95 cm^{-1} is due to the C-N stretching of aromatic amines. ZnO show strong absorption peak in the range of $400-500\text{ cm}^{-1}$.

4.5 Photo catalytic experiments for degradation of dye:

As already explained that methyl orange in water can be treated by photo catalysis using $g-C_3N_4$. But photo catalytic activity of $g-C_3N_4$ is limited due to the high recombination rate of electron and hole. In our present work $g-C_3N_4$ composite with ZnO is prepared to increase its photo catalytic activity [22]. We carried this test by stirring 0.2 gm of of each composite with 25 ml of methyl orange solution for one hour in absence of light. Then we collect the sample solution after centrifuging it. Again we stirre the solution by applying light irradiation and we collect the sample after certain intervals of time. And then we take UV-visible spectra of the above samples.

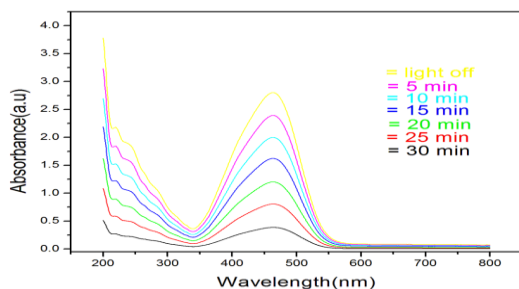


Fig 6 (a): UV-visible absorbance of methyl orange after the treatment with $g-C_3N_4-ZnO(C)$ at different time intervals.

From the above figure it is clear that after the treatment of

aqueous solution of methyl orange with $g-C_3N_4-ZnO(C)$ methyl orange shows significant absorption.

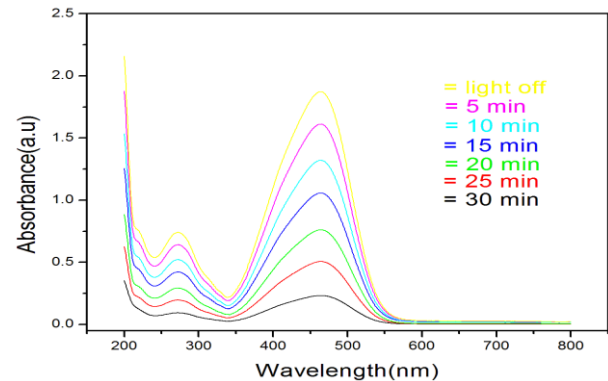


Fig. 6(b): UV visible absorbance of aqueous methyl orange solution after the treatment with $g-C_3N_4-ZnO$ (In situ)

Comparing the graph in Fig 6(a) and Fig 6(b) we can conclude that degradation is greater in presence of $g-C_3N_4-ZnO$ (In situ) composite. Because when $g-C_3N_4-ZnO$ (In situ) is used as photocatalyst methyl orange show lower absorption peak.

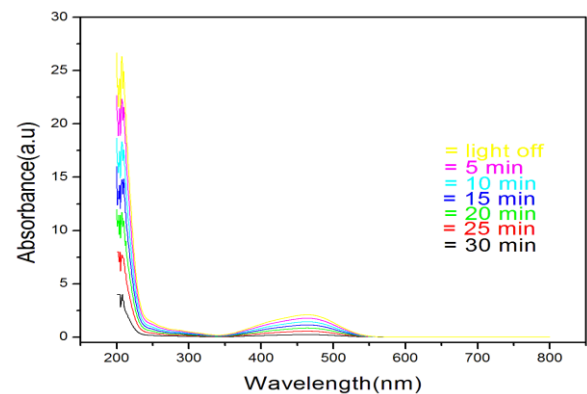


Fig. 6 (c): UV-visible absorbance graph of methyl orange when treated with $g-C_3N_4-ZnO$ (H).

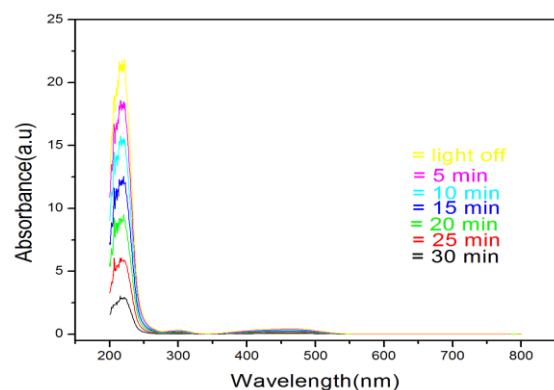


Fig. 6(d): UV-visible absorbance of methyl orange in presence of $g-C_3N_4-ZnO(N)$ photo catalysts.

From the above UV-Vis absorbance graph we may conclude that among the prepared photo catalysts $g-C_3N_4-ZnO(N)$ is more efficient and it can be used for dye degradation. Since from the fig:5(d) it is cleared that in presence of $g-C_3N_4-ZnO(N)$ methyl orange show nearly zero absorbance so it is a better photo catalyst among the prepared photo catalysts. When semiconductor is prepared at the nano level it enhances the photo catalytic activity [23]. In our present investigation we used different method to prepare different sizes and morphologies of ZnO and it helps to increase the photo catalytic property of ZnO.

5. CONCLUSIONS:

The conclusions obtained from the present work are summarized here. The present study involves the synthesis of $g-C_3N_4, ZnO$ and various $g-C_3N_4$ composite with ZnO. Photo catalytic degradation of methyl orange in water was studied by using the prepared composites. It can be concluded that photo catalytic efficiency of $g-C_3N_4$ is increased by preparing composites of this $g-C_3N_4$. From the dye degradation graph we may conclude that photo catalytic activity of $g-C_3N_4-ZnO(N)$ is greater than the other composite. It means electron-hole separation is maximum in $g-C_3N_4-ZnO(N)$. Hence it shows high dye degradation property. This investigation may provide guidance for the morphology-controlled synthesis of ZnO nanostructures and their application in the treatment of organic pollutants.

6 REFERENCES

- [1] K.Sayama., H.Hayashi, T.Arai, M.Yanagida, T.Gunji, H.Sugihara. Highly active WO_3 semiconductor photo catalysts prepared from amorphous peroxy-tungstic acid for the degradation of various organic compounds. *Appl. Catal. B: Environ* 2010, 94, 150-157.
- [2] Wang.X, S.Blechert, M. Antonietti polymeric $g-C_3N_4$ for heterogeneous photocatalyst. *ACS Catal* 2012, 2, 1596-1606.
- [3] Noto.V.D, Negro.E. Development of nanocatalysts based on carbon nitride support for ORR process in PEM fuel cells. *Electrochim. Acta* 2010, 55, 7564-7574.
- [4] Kamat.V.Prashant. Environmental Photochemistry on Semiconductor surfaces. Visible light induced Degradation of a Textile Diazo Dye, Naphthol Blue Black on TiO_2 Nanoparticles. *J.Phys. Chem* 1996, 100, 8436-8442.
- [5] More. A.T, Vira.A, and Fogel. S. Biodegradation of trans-1, 2-dichloroethylene by Methane Utilizing Bacteria in an Aquifer Simulator, *Environ. Sci. Technol.* 23, (1989), 403-406.
- [6] Patil.V.B, Mohabansi.N.P, Yenkie.N.A Comparative study on photo degradation of methylene blue dye effluent by advanced oxidation process by using TiO_2/ZnO photo catalyst. *RASAYANJ. Chem* 2011, 4, 814-819.
- [7] Arslan.I, Balcioglu. I.A, Tuhkanen.T, Bahnemann .D. $H_2O_2/UV-C$ and $Fe^{2+}/H_2O_2 /UV -C$ versus $TiO_2/UV -A$ treatment for reactive dye wastewater, *J. Environ. Engg* 200,126,903-911
- [8] Chowdhury. P, Goma , H Ray AK. Dye – Sensitized Photocatalyst: A Breakthrough in Green Energy and Environmental Detoxification. *ACS Symposium series* 2013,1124,231-266.
- [9] Kumar,R, Kumar ,G. and Umar, A.ZnO Nano Mushrooms for Photo catalytic degradation of Methyl Orange. *Materials Letters* 2013, 97, 100-103.
- [10] D.A. Tryk, A. Fujishima, K. Honda, *Electrochim. Acta* 45 (2000) 2363.
- [11] Daneshvar.N, Aber.S, Hosseinzadeh.F. Study of Acid Orange 7 Removal in Contaminated water by Photo oxidation Processes. *Global NEST Journal* 2009, 10, 16-23.
- [12] Chen.T, Zheng.Y, Lin.J.M, Chen.G. Study on Photo catalytic Degradation of Methyl orange in Water using Ag/ZnO as catalyst by Liquid Chromatography Electroscopy Ionization Ion – Trap Mass Spectroscopy. *J Am Soc Mass Spectrum* 2008,19,997-1003
- [13] Roselin. S, Rajarajeshwari.G.R, Selvin.R, Sivasankar.B, Rengarag.K. Sunlight/ ZnO – Mediated Photo catalytic degradation of Reactive Red 22 Using Thin Film Plate Bed Flow Photo reactor. *Solar Energy* 2002, 73, 281-285.
- [14] Chakrabarti .S, Dutta. B. K. Photo catalytic degradation of modern textile dye in waste water using ZnO as semiconductor catalyst. *J. Hazard Mater* 2004,112,269-278.
- [15] Wang.X, Maeda.K, Thomas.A, Takanabe.K, Carlsson.J.M, Domen.K, Antonietti M. A metal free polymeric photo catalysts for hydrogen production from water under visible light. *Nat Mater* 2009, 8, 76-80.
- [16] Yan. S. C, Li .Z. S, Zou .Z G. Photo degradation performance of $g-C_3N_4$ fabricated by directly heat iming melamine. *Langmir* 2009, 25(17), 10397-10401.
- [17] Hussin. F, Lintang H. O, Yuliati. L. Enhanced activity of $g-C_3N_4$ with addition of ZnO for photo catalytic removal of phenol under visible light. *Malaysian Journal of Analytical Sciences* 2016, 20, 102-110.
- [18] Yuan. X, Zhou, Jing Q, Tang. Q, Mu Y, DuA.K. Facile synthesis of $g-C_3N_4$ Nanosheets /ZnO nanocomposites with enhanced photo catalytic activity in reduction of aqueous Cr(VI) under visible light. *Nanomaterials* 2016,6 173 -179.
- [19] Suresh Sandhu.JS. ZnO nanobelts :An efficient catalyst for synthesis of 5-arylidine -2,4 – thiazolidinediones and 5-arylidine -2-rohdanines. *International Journal of Organic Chemistry* 2012,2 305-310.
- [20] McMurdieH, MorrisM, EvansE, ParetzkinB, Wong–Ng,W, Ettlingerl, HubbardC. *Powder Diffraction* 1986, 1, 76.
- [21] Li.X, Zhang .J, Shen.L, Ma.Y. Preparation and Characterization of $g-C_3N_4$ through pyrolysis of melamine. *Appl Phys* 2009,94,387-392

- [22] Wang .Y, Shi.R, R.Lin. Enhancement of Photocurrent and photo catalytic activity of ZnO hybridized with g-C₃N₄.Energy and Environmental Science 2011, 4(8), 2922-2929.
- [23] H.Gerischer. Photo electrolysis catalysis of the oxidation of organic molecules by oxygen on small semiconductor particle with TiO₂ as an example. Electro chemica Acta 1993, 38, 3-9.