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Der Pharma Chemica, 2015, 7(10):391-397
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

AgI-ZnO: A novel plasmonic photocatalyst for decomposition of mythylene blue dye

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ABSTRACT

A novel plasmonic photocatalyst, AgI-ZnO, has been prepared using precipitation followed by hydrolysis method. Its photocatalytic activities were studied for degradation rate of methylene blue (MB) dye with respect to time in visible and UV radiation. On the basis of results, it is concluded that visible irradiation is more efficient for the degradation of the dye as compared to UV radiation. Thus AgI impregnation can be demonstrated to be a proficient strategy to improve the photocatalytic performance of ZnO photocatalysts and such improved photocatalyst can be successfully used for abatement of dye pollutants from polluted water. The newly synthesized catalyst was characterized by X-ray diffraction, TGA, EDX and SEM studies.

Keywords: AgI-ZnO nanostuctures, visible spectrum, methylene blue, photo catalytic degradation, Ag Nanoparticles

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INTRODUCTION

Water contamination amputation of organic dyes in the effluents of textile plants is of immense environmental concern due to the potentially toxic effects of relatively small amount of these compounds [1]. Organic compounds are broadly used in industries and in daily life, have become regular pollutants in water bodies. As they are known to be lethal and carcinogenic, an effective economic treatment for eliminating the organic pollutants in water has been found to be an insistent demand. Environmental and energy issues are the most important concerns faced by human beings. Organic pollutants released from industrial wastes are highly toxic even at relatively low concentration, and thus can cause severe diseases in human beings [2-4]. Photocatalysis under sunlight is promising way for the removal of water contaminants because of its abundant, cheap and clean characteristics [5-6]. TiO_2 and ZnO are well known conventional semiconductors having wide band gap [7-11]. From the last decade, a considerable number of new photocatalytic materials have been developed as potential substitutes of a TiO_2 [12]. Comparatively ZnO semiconductor has many advantages over TiO_2 semiconductor such as low cost, low toxicity, easy to prepare and high photocatalytic activity for degradation of dyes [13-15]. Doping of oxide semiconductor with Ag nanoparticales(nps) improves its photocatalytic property [16]. The revolutionary work on TiO_2 photochemical electrode for water splitting under UV radiation achived by Fujishima and Honda, boosted a wave of semiconductor photocatalysis of TiO_2 based materials worldwide.

In this scenario, Ag nps with inimitable surface plasmon resonance property have fascinated much attention recently in the field of photo catalysis. Ag halides, classical photosensitive materials in photographic film, are potential photocatalysts due to their narrow band gap of 2.25 ev. Recently the binary Ag/AgX photocations have been designed to improve photocatalytic activities of the photocatalysts [17]. In situ oxidation reaction between Ag nano-wires and $FeCl_3$ solution [18-20] have generated Ag/AgCl core structure which exhibited excellent photocatalytic activity for decomposition of methyl orange dye under visible light irradiation.

Keeping in view the importance of Zn and Ag nps in photocatalytic activity, a new modified plasmonic photocatalyst has been developed and its photocatalytic activity for MB dye decomposition has been studied and reported in the present research article.

MATERIALS AND METHODS

All chemicals used during the investigation were of either AR or chemically pure grade. Double distilled water was used throughout the experiments.

2.1 *Preparation of ZnO Nps [21]*

200ml of 0.4M aqueous solution of sodium hydroxide was heated up to 55^{o}C stirred on magnetic stirrer for 45 min. Into this solution 100 ml of 0.45M aqueous solution of zinc nitrate was added drop wise with constant stirring for 60 min. The reaction mixture was kept under stirring at 55^{o}C for 2h.The completion of reaction was confirmed by observing white precipitation in the reaction mixture. The reaction mixture was filtered, washed with deionized(DI) water followed by ethanol. The product was dried under vacuum.

2.2 *Preparation of AgI - ZnO composite Nps.*

In 100 ml beaker 20 ml 0.04 M $AgNO_3$ solution was taken and 20 ml 0.04 M of KI solution was added into it drop wise with constant stirring for 60 min to form the AgI suspension. This AgI suspension and Zinc nitrate solutions were added simultaneously in to 100 ml beaker containing 0.4 M alkali solution and kept for 2 hrs at 55^{0}C with constant stirring. Completion of reaction was confirmed by formation of precipitate. The reaction mixture was filtered, washed with DI water followed by ethanol. The product was dried under vacuum.

2.3 Photocatalyst reaction

100 ml of methylene blue dye (MB) dye solution was taken in the reactor (Fig.1). Desired pH of the solution was adjusted using 0.01M NaOH and 0.01M H_2SO_4. 300 mg of newly prepared and characterized AgI-ZnO photocatalyst was added in to the dye solution. Halogen lamp (500 Watt) was used as a source for visible radiation. The photocatalytic process was continued for 280 min. The concentration of MB solution was measured at certain time intervals using CE 2371 spectrophotometer.

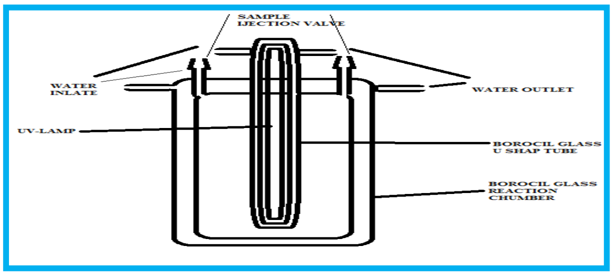

Fig. 1. The Photoreacter

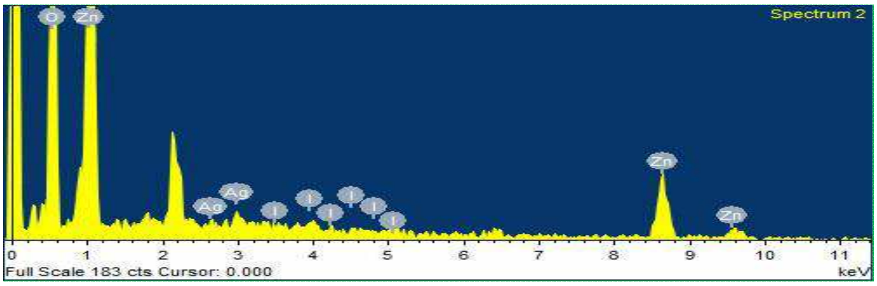

Fig. 2 EDX spectra of AgI-ZnO photocatalys

3. RESULTS AND DISCUSSION

3.1 *Morphology and structure of nanostructured AgI-ZnO photocatalyst*

EDX, XRD and SEM Studies

The newly synthesized AgI-ZnO composite photocatalyst was characterized using EDX and XRD spectroscopy. EDX spectra (Fig.2) confirm the presence of Zn, O, Ag and I in the nanophotocatalyst material. Fig.3a and 3b represents the XRD patterns of the ZnO and newly prepared AgI-ZnO composite nanophotocatalyst respectively. Fig. 3a shows the peaks at 2θ of 31.8°, 34.5°, 36.4°, 47.6° and 56.7°, correspond to the crystal planes (100), (002), (101), (102), and (110) of ZnO indicate the presence of crystalline hexagonal ZnO phase (hexagonal structure; JCPDS: 36−145). In Fig. 3b, the peaks apeared at 2θ values 18.81, 23.77, 38.81correspond to AgI phase [22]. Comparison of XRD spectra of pure ZnO and AgI-ZnO(Fig.3a & 3b) confirms the loading of AgI on ZnO and thus successful synthesis of new AgI-ZnO nanophotocatalyst material.

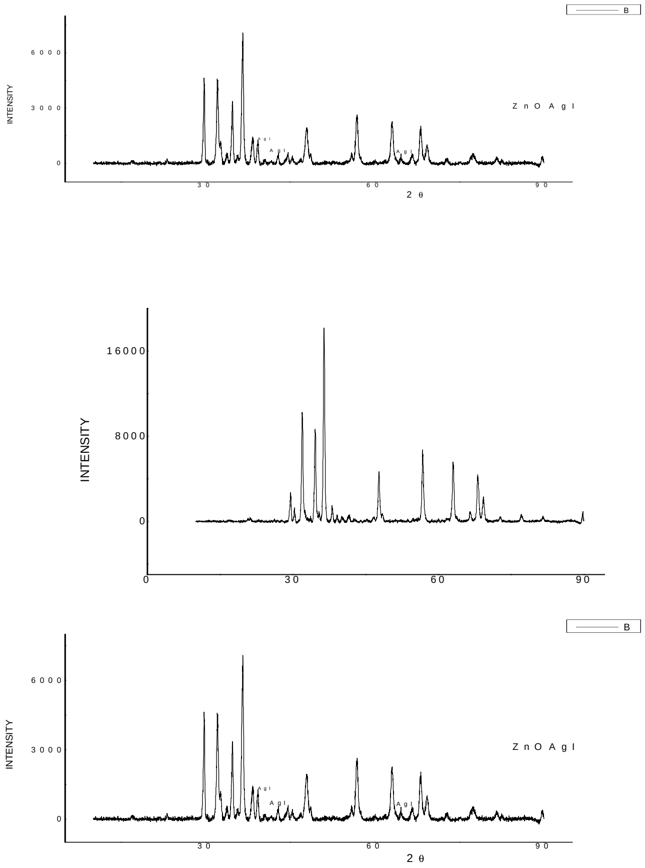

Fig. 3. (a) XRD of pure ZnO photocatalyst; (b) XRD of AgI-ZnO photocatalyst

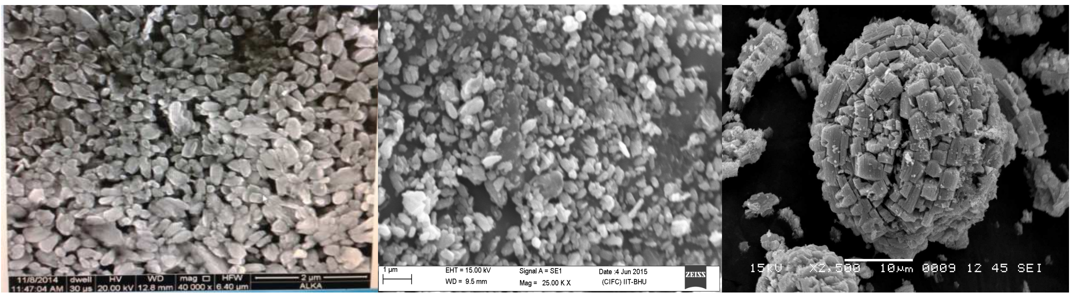

Fig. 4 a) SEM image of AgI-ZnO composit, b) SEM image of AgI-ZnO composit containing small white shiny crystals of ZnO and AgI, c) Foot ball shape SEM image of AgI-ZnO composit in agrigated form

SEM images of the AgI-ZnO Nps have been shown in Fig.4 (a), (b) and (c). The crystallization process and crystal size of ZnO does not affected by modification process. The average crystal size of ZnO nanoparticles calculated using schemer formula was found to be 52.17 nm (nanoscale particle) in size and that of foot boll shape aggregated AgI-ZnO photocatalyst, Fig. 4(c), is in the range of 10−30 nm. After modification by AgI, Fig. 4(b), the surface morphology and size of the sample have no remarkable change and AgI-ZnO nanomaterials. The SEM micrographs confirm the successful synthesis of the composite nanophotocatalytic material.

Thermogravimetic Studies

The thermo gravimetric analysis (Fig.5) indicates that the first derivative peak at 80.30^{0}C with 4.2% weight loss of the material may be due to release of some unknown easily evaporable matter like moisture. There is no weight loss between the temperature ranges of 80.30^{0}C to 586.02^{0}C shows the photocatalytic material is thermally quite stable. The maximum weight loss i.e. 19.8 % (exactly corresponding to the mass of ZnO) occurred at second derivative peak at the range 586.02^{0}C to 711.82^{0}C appears to be because of the successive loss of ZnO from the composite. The residue left behind after 711.82^{0}C exhibits slow rate of thermal decomposition

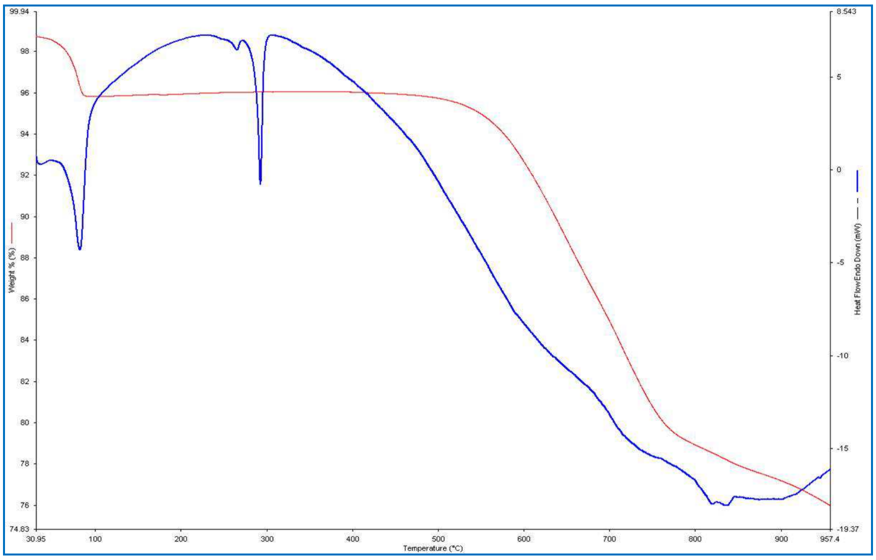

Fig 5: TGA of AgI-ZnO nanophotocatalys

3.2 Photocatalytic Reaction

As a model reaction we performed reaction of AgI-ZnO photocatalyst (300 mg) with 100 ml of M.B. dye (25ppm). After magnetic stirring at room temperature in dark for 1 hr, 10 ml of reaction mixture was taken out, centrifuged and filtered by using Watmann filter paper No. 64. The filtrate was taken for measuring remaining concentration of MB dye using UV-VIS spectrophotometer and the degradation ratio was calculated using the equation

$$D = \frac{(I_0 - I)}{I_0} \times 100\%$$

(Where, I_0 and I are initial and final concentrations of MB dye; D is degradation rate.)

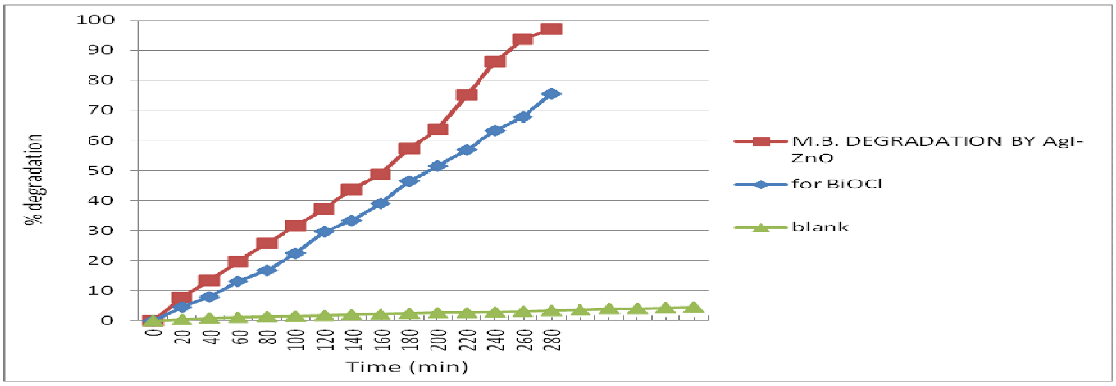

Fig. 6 Comparison of degradation of MB dye in absence (blank) and presence of AgI-ZnO and BiOCl photocatalyst

The photocatalytic activity of the catalyst was evaluated by photocatalytic degradation of MB aqueous solution under visible light irradiation. The initial concentration of MB taken was 25 ppm and amount of photocatalyst used was 300 mg/100 ml. In the absence of photocatalyst the degradation MB dye was 4.42% only.

It can be noticed that (Fig.6) that AgI-ZnO photocatalyst degrades the MB dye upto 97.0 % within 280 min. of time interval. If compared with degradation rate of well known photocatalyst, BiOCl Nps[23], it is clear (Fig.6) that AgI-ZnO possesses higher photocatalytic activity for MB degradation under visible light irradiation. Thus it can be concluded that AgI-ZnO is a new potentially able plasmonic photocatalyst for degradation of organic pollutants, like MB dye.

3.3 Effect of pH

The pH is considered to be one of the most important parameter that can affect the photo catalytic oxidation processes. Influence of pH on degradation of MB is presented in Fig.7. The initial pH of dye solution was varied from pH 2-12. The studies were carried out with 25 ppm Methylene Blue dye solution and 300 mg/100 ml of catalyst dose. It is quite evident from the graph that as the pH of dye solution changes from acidic to alkaline; the percentage degradation increases. This implies that alkaline condition is more favorable for photocatalytic degradation of the dye which may be due to easy formation of the reactive intermediates that is hydroxyl radicals, which further help in enhancing the photo degradation reaction rate.

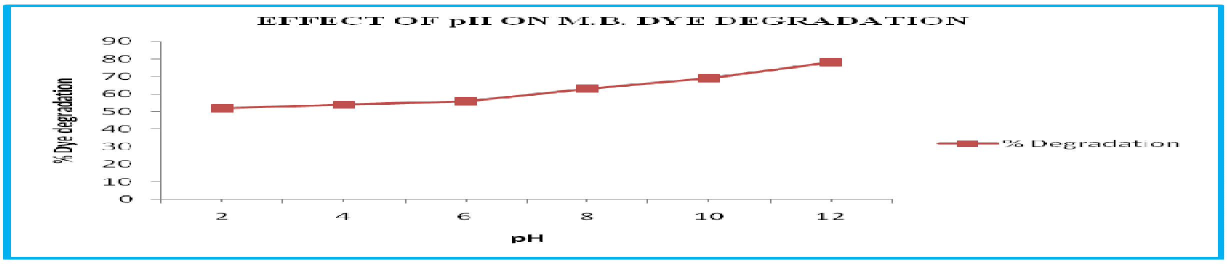

Fig.7. Effect of pH on Methylene Blue(MB) dye degradation

3.5 Effect of Catalyst Dose

The catalyst dose is another important parameter which has strong influence on the degradation kinetics of dye solution. AgI-ZnO photocatalyst was used in slurry mode. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of AgI-ZnO catalyst varying from 100 to 600 mg/100ml, with 25 ppm dye solution. The graph depicts that as the concentration of catalyst increases from 100 to 300 mg/ 100ml the percentage degradation also increases from 52% to 87%. But on further increasing the catalyst concentration from 300 to 500 mg/ 100ml, the percentage degradation gradually decreases from 87% to 53%. So maximum degradation rate has been observed with catalyst dose of 300 mg/100 ml and it was considered as the optimum dose for the degradation of methylene blue dye solution (25 ppm) for subsequent analysis. Initial increase in degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of light is absorbed in the beginning, accelerating the process. When all the dye molecules were adsorbed on AgI-ZnO no improvement was achieved by adding more catalyst. The decrease in efficiency, which is observed in the (Fig. 8), may be due to increase in opacity of the suspension and enhancement of the light reflectance, because of the excess of AgI-ZnO particles.

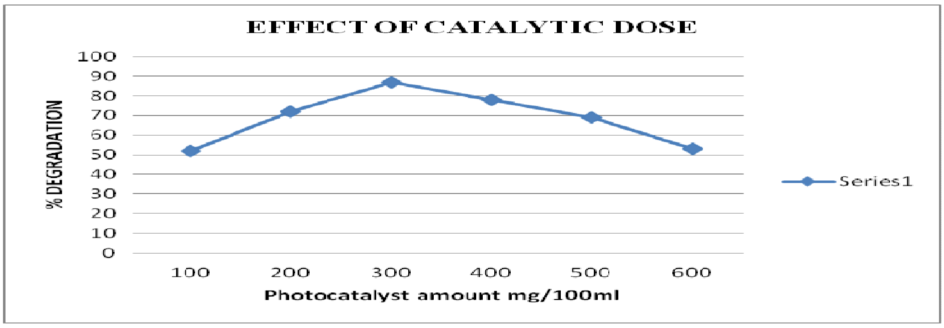

Fig.8. Effect of catalytic dose on M. B. dye degradation

The effect of photo reduction time of AgI-ZnO on the photocatalytic degradation of MB was examined to test the usefulness of photo catalyst and its stability which is rather important for its practical application. Fig. 9 shows the reusability of AgI-ZnO catalyst for MB photocatalytic degradation. Although the degradation ratio of MB decreases to some extent after each run, the catalyst still exhibited efficient activity with about 84.2% of the degradation ratio up to six run. Thus the self prepared new nanophoto catalyst could retain 84.2% of the initial activity for recycling run suggesting very good stability and reusability of AgI-ZnO plasmonic photocatalyst under present investigation.

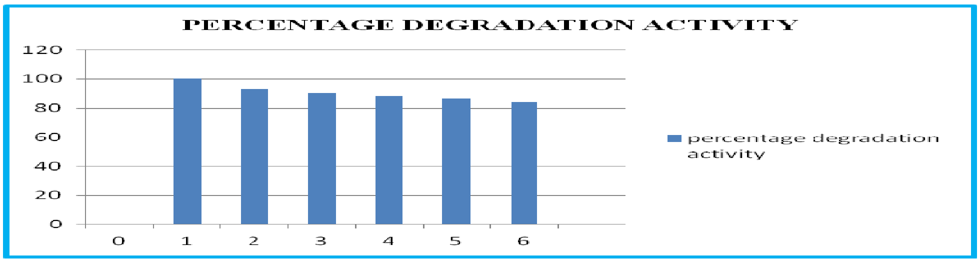

Fig. 9. Reusability of AgI-ZnO catalyst for MB photocatalytic degradation under visible light irradiation. MB initial conc. of 25 ppm, catalyst dose 300 mg/100 ml and reaction time of 2h

CONCLUSION

A novel ZnO-AgI composite plasmonic photocatalyst was prepared by the hydrothermal followed by precipitation method. The composite photocatalyst exhibits the absorption in both UV as well as visible region due to plasmonic effect of AgI Nps and UV response due to ZnO Nps. Photocatalytic activity was found to be significantly enhanced under visible light irradiation and have shown good plasmon effect for the enhanced activity. The nanophotocatalytic material under investigation has been proved to be successful for degradation of dyes like MB. Moreover catalyst under study could retain 84.2% of the initial activity after recycling run suggesting AgI-ZnO has good stabled reusable properties. Thus the new nanophotocatalytic material can be successfully used for control of water pollution.

Scope for further work

Looking at outstanding photocatalyst performance of the photocatalytic material under study the work can be extended to test its photocatalytic activity for degradation of other organic pollutants like benzene, benzopyrene, toluene, and other dye pollutants etc.

Acknowledgements

The authors gratefully acknowledge the support of the UGC project, for providing financial assistance, CSIR NEERI Nagpur for providing E-library facilities for literature survey. Thanks are due to the Director IICT Hyderabad for help in EDX, XRD, and SEM studies. Special thanks are extended to Dr. Brijesh Pare, Department of chemistry, Madhav Science P.G. College, Ujjain, for his valuable guidance during the investigation. Authors are grateful to the principal of Hislop College Nagpur for providing research laboratory and library facilities. RRK is thankful to the principal, C. J. Patel College Tirora for his moral support during the course of this investigation.

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