International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Special Issue 38 (February, 2016), PP. 9-12

PHOTOCATALYTIC ACTIVITIES OF COPPER DOPED ZNO-ZNS NANOPARTICLES FOR THE DEGRADATION OF METHYL ORANGE

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Abstract— **Degradation of dyes is a standard method to check the photocatalytic activity of any type of photo catalyst. Photo catalytic degradation materials such as ZnO, ZnS have been studied because of high photochemical reactivity, H_2 production, hexagonal wurtzite / zinc blende structure and nontoxic nature. In this report the photo catalytic property of ZnO and ZnS nanoparticles separately and the combination of ZnO-ZnS ($ZnO_{0.5}S_{0.5}$) and the copper dopped ZnO-ZnS nanoparticles, which are synthesised by simple solvothermal method are investigated. Methyl orange (MO) is taken as a model organic compound. The percentage of degradation is calculated. It is found that the % of degradation is improved in the combined ZnO-ZnS nanoparticles system while comparing to the individual ZnO , ZnS nanoparticles. However the copper doped ZnO-ZnS nanoparticles show much degradation percentage comparing to the others. These results indicate that the copper doped ZnO-ZnS nanoparticles can be a good choice for the treatment of organic waste-water in future.**

Index terms- **Photocatalytic activity, ZnO-ZnS nanoparticles, solvothermal, methyl orange (MO), degradation percentage.**

I. INTRODUCTION

Waste water management faces a real challenge recently. Water is contaminated from the waste released from the industries [1]. To reduce the negative impact of the serious environmental problems due to the pollutants created many techniques such as filtration, chlorination, ozonization etc have been developed [2]. In the recent years it has been experimented and proved that semi-conductors which mediated photocatalytic oxidation of organic compounds, is a successful alternative to conventional methods for the removal of organic pollutants from water [3]. As an important II–VI group semiconductors, Zinc oxide (ZnO) ,Zinc sulphide (ZnS) etc are studied intensively because of their wide application in the photonic and electronic field. They are used as photocatalyists [4-7], solar cells [8], gas sensors [9] and photo-detectors [10].

In the present study the photocatalytic application of ZnO and ZnS nanoparticles which are synthesised by simple solvothermal method is studied. In a photocatalytic system, photo-induced molecular transformation or reaction takes place at the surface of the catalyst. Basically electron-hole pair formation starts the photocatalytic activity. The electron-hole pair is generated when a photocatalyst is illuminated by the light stronger than its band gap energy. Electrons are generated in the valance band (VB) and migrates from the valance band (VB) to the conduction band (CB) creating holes in the valance band. The holes can generate hydroxyl radicals which are highly oxidizing in nature that can react with dye molecule and abstract electron from dye molecule and thus the process of degradation starts [11-15]. Hydroxyl and superoxide radicals are formed as the small size ZnO nanoparticles have increased specific surface area and more numbers of active surface sites.[16-19] However, there is a possibility for the agglomeration which leads to the loss of active site and may reduce the photocatalytic efficiency and the photo-oxidation rate of organic compounds [20-21]. It is desirable to improve this drawback simply by an effective method. ZnS which has a hexagonal/ cubic structure, is one of the most widely investigated photocatalysts because it rapidly generates electron-hole pairs under photoexcitation, as well as the property of exhibiting a relatively high activity for H_2 production under UV light [22, 23]. To ensure overall catalytic efficiency, sophisticated controls are required to obtain a balance between size (for stability) and activity.

In the present work the photocatalytic property of the synthesised ZnO, ZnS nanoparticles and the combined ZnO-ZnS ($ZnO_{0.5}S_{0.5}$) is studied with the help of the degradation of methyl orange. High elctrochemical stability and higher number of electron mobility are necessary for the high efficiency of photo degradation. The effect of copper doped ZnO-ZnS nanoparticles which help in maintaining the high efficiency of photocatalytic activity is also studied.

II. EXPERIMENTAL SETUP

A. Synthesis of ZnO-ZnS nanoparticles

ZnO-ZnS nanoparticles are prepared by adopting Mahadevan's method [24].

Zinc chloride (used as the precursor) and urea/ thiourea are dissolved in 100 ml of ethylene glycol and irradiated with microwave for 30 minutes using a domestic microwave oven (Frequency 2.45 GHz and power 800 W). The resulting white precipitate was first washed with de-ionised water several times and then with acetone and dried in atmosphere. The same method is adopted for the synthesis of Cu $^{2+}$ doped ZnO-ZnS nanocomposites. Two mole percentage (0.05, and 0.1) of copper chloride is mixed well using a magnetic stirrer to the precursor to synthesise the copper doped ZnO-ZnS nanoparticles .X-ray powder diffraction, scanning electron microscopic techniques are used for structural chacterization of the nanoparticles.

B. Photocatalytic Experiments

In this photocatalytic experiment, 50 ml of 10ppm methyl orange dye solution prepared using deionized water is taken in a 200ml borosil beaker. A mass of 50mg of nanopowder is dispersed well in this solution by stirring the solution using magnetic stirrer. After 30 min of dark adsorption, the photo reaction beaker is exposed to the UV irradiation which is produced by an 18 W high pressure UV-AB Hg lamp which is set in a self assembled chamber. During the photocatalytic reaction, all the other light sources are isolated. Then 5 mL of the liquid sample is taken at the top of the vessel at a fixed time interval of 30 minutes. The samples are centrifuged at 3,000 rpm for 3 min before subjected to UV-Vis absorption spectroscopic analysis.

III. 3. RESULT AND DISCUSSION

The XRD pattern observed are shown in Figure 1. In figure 1(a), all the diffraction peaks can be indexed to zinc oxide with hexagonal würtzite structure with an particle size less than 40nm. Figure 1(c) shows that all the diffraction peaks could be matched with the cubic zinc sulphide peaks. The particle size is approximately 20nm. In the other figures 1 (c), (d) (e) the peaks are of mixed phase indicating the formation of both zinc oxide and zinc sulphide. The figure 1 (d) & 1 (e) the xrd pattern shown are for the copper doped ZnO-ZnS nanoparticles. The particle size of the copper doped ZnO-ZnS nanocomposites is also calculated and found to be less than 5nm.

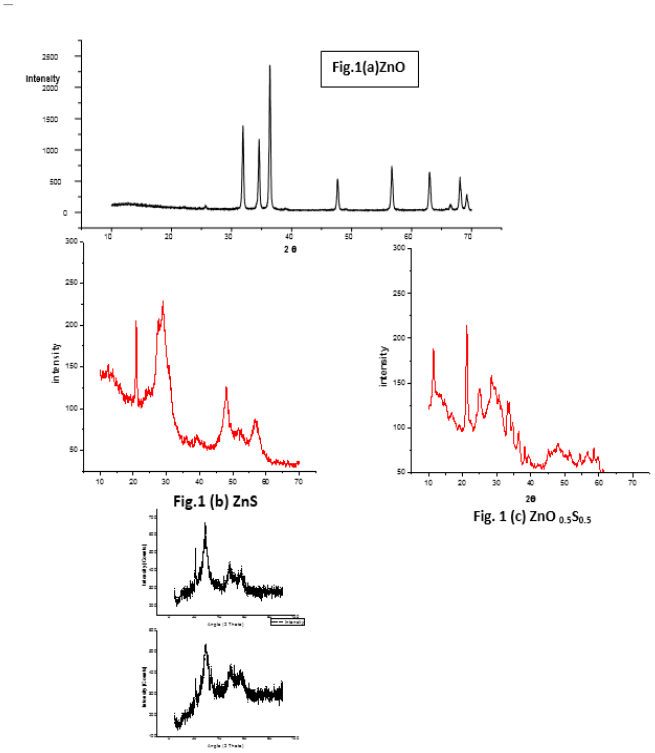

Fig. 1 (d) ZnO-ZnS: Cu^{2+} doped(0.05%) Fig. 1(e) ZnO-ZnS: Cu^{2+} doped(0.1%)

Figure 1 XRD patterns obtained for the samples

The SEM images of all the samples are given in Fig. (2). The images show the agglomeration and confirms the formation of ZnO, ZnS, ZnO-ZnS nanoparticles.

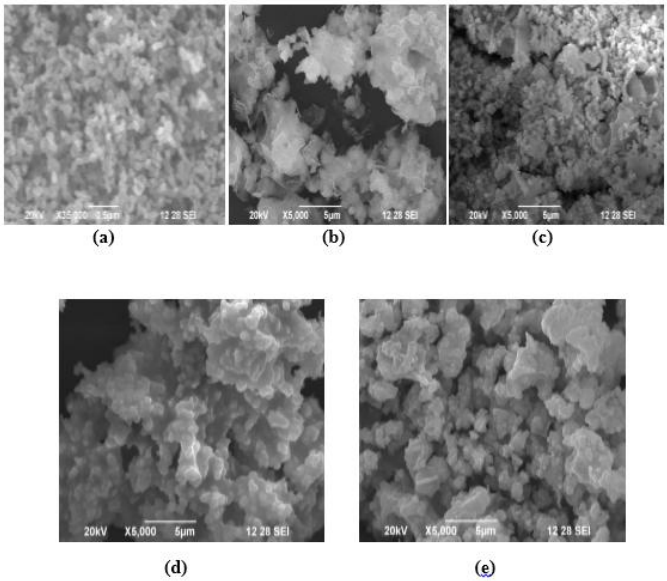

Figure 2 SEM images (a) ZnO (b) ZnS (c) ZnO $_{0.5}$ S $_{0.5}$ (d) ZnO $_{0.5}$ S $_{0.5}$:Cu^{2+}(0.05%) (e) ZnO $_{0.5}$ S $_{0.5}$: Cu^{2+}(0.1%)

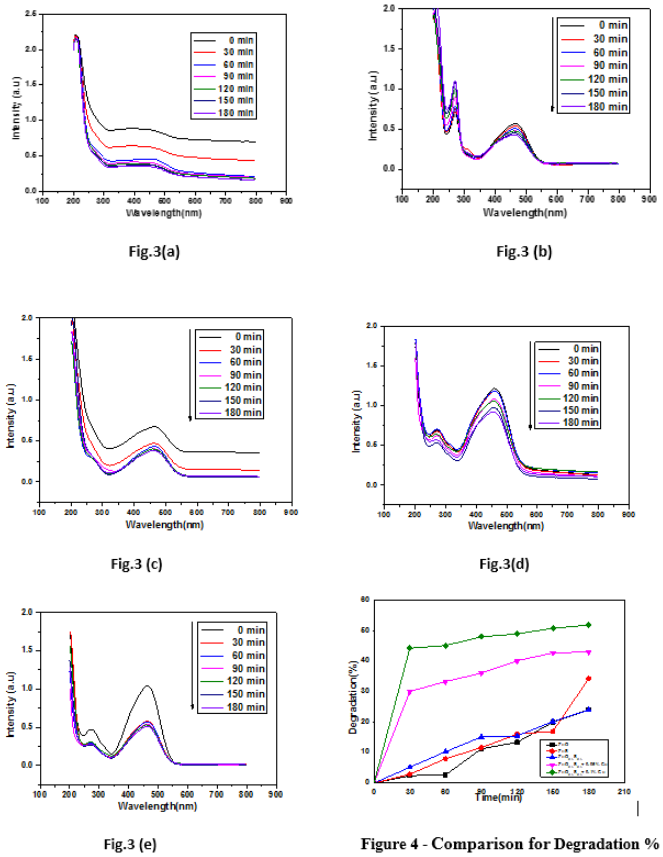

Figure 3 UV–Visible absorption spectra at different reaction time

(a) ZnO (b) ZnS (c) ZnO $_{0.5}$ S $_{0.5}$

(d) ZnO $_{0.5}$ S $_{0.5}$:Cu^{2+}(0.05%) (e) ZnO $_{0.5}$ S $_{0.5}$: Cu^{2+}(0.1%)

The photocatlytic study explains that the chemical stability of the photocatalysts. We investigated the photocatalytic activity of ZnO-ZnS nanoparticles after prolonged exposture to the UV light in aqueous solution. The effect of morphology on the photodegradation efficiency can be ascribed to the following reason; when the size of the nanoparticles decreases, the amount of the dispersion particles per volume in the solution will increase which results in the enhancement of the photon absorbance.[25] The intensity of absorption spectra decreases as the exposure time increases from 0 to 3 h. The intensity of the main

absorption peaks decreased due to the degradation of reactive methyl orange.

Percentage degradation of MR was calculated using the relation:

% degradation= $[(A_0-A_t)/A_0] \times 100$ ----------(1)

where A_0 is absorbance of dye at initial stage, A_t is absorbance of dye at time "t".

A graph is drawn between time Vs the percentage of degradation (Figure 5) to show the photo degradation results. The percentage of degradation is more for ZnS than that for ZnO. In the ZnO the hydroxyl formed in the ZnO, agglomerates and there is less electron-hole pair. But in ZnS the The ability of producing the photocatalytic hydrogen generations enhances the electon-hole pair and there is an increase in the photo-degradation percentage. When we compare the combined system of ZnO-ZnS with those ZnO and ZnS there is a possiblity of increase in number of electron in the conduction band and therefore the degradation percentage is increased. This is motivated further when a dopant like copper is used. We see the percentage of degradation increases in the case of copper doped ZnO-ZnS nanocomposite as it is indicated in figure. Also it is noted as the percentage of copper increases the percentage of degradation is also increased. This is well understood that the addition of copper which acts as a capping agent, breaks the agglomeration and the recombination of electron-hole pair and enhances the phocatalytic property.[26]

IV. CONCLUSION

Sythesising ZnO-ZnS nanocomosite by a simple solvothermal method is a simple and cost effective method. Combing ZnO and ZnS enhances the photocatalytic activity and it could be used in future for the waste water management. Addition of copper to ZnO-ZnS nanocoposites still increase the electrons in the conduction band and enhances the photo degradation process.

V. ACKNOWLEDGEMENT

The author G.JanitaChristobel thanks the UGC for the Post Doctoral Award (Women)

F15-149 /12 (SA-II)

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