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Environmentally Sustainable Visible Photocatalytic Nanostructured ZnS Doped with CuS for Chemical Effluent Treatment Applications

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Abstract

Owing part of the innovative research concerning the degradation of the chemical industry pollutants was notably focused on photocatalysis process, in order to meet the strict pollution abatement legislation required by environmental protection agencies worldwide. Nanostructured TiO₂, ZnO and ZnS as a semiconductor photocatalysts have proved to be effective and more suitable for the widespread environmental application, such as air purification, water disinfection, hazardous waste remediation and water purification. In the present investigation, CuS doped ZnS nanopowders have been synthesized by simple and cost effective sol-gel process. The dried powders have been sintered and the visible photocatalytic property of the pure ZnS and CuS doped in ZnS have been tested for the degradation of standard dyes along with chemical effluent. The samples have been characterized for their structural, chemical and morphological properties by employing X-ray Diffraction (XRD), X-Ray Photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM) techniques, respectively in order to understand the structure–property relationship.

Keywords: sol-gel process; nanopowders; chemical effluent; sustainability; visible photocatalytic process; sintering

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1. Introduction

Photocatalysis is a process wherein free radicals are generated by the creation of electron-hole pair by absorption of light greater than or equal to its bandgap. The generated free radicals are excellent oxidizers [1]. Advanced water treatment technologies have been developed in the past two decades to address environmental issues. Yet, removal of organic pollutants such as dyes from textile and various other industrial effluent has remained a challenge [2, 3]. Photocatalytic degradation is a quick oxidation technique which is highly efficient and cost effective for water treatment [4].

TiO₂ has been widely researched as a primary material for industrial effluent treatment. Research in this area has also shown that doping is a process of increasing the photocatalytic activity of titanium with metals such as iron, bismuth, cerium, manganese, nickel and copper [4-10]. Other materials such as sulfides of Zinc, Cadmium, Tin, and Molybdenum are also under investigation for photocatalytic activity. They have also been doped with other materials such as Nickel, Iron, Cerium to enhance their photocatalytic activity [10]. Zinc sulfide has shown to release Hydrogen gas from a suitable substrate by photocatalytic activity [11, 12]. Nano – semiconductors have attracted heavy research for their enhanced photocatalytic activity due to their high surface area to volume ratio. This, in turn, increases the bandgap leading to enhanced redox potential. Hence, they have higher photocatalytic activity [10].

Recently, ZnS: CuS microspheres were synthesized and were proved to show photocatalytic activity on rhodamine B [13]. In the present investigation, CuS doped ZnS nanopowders have been synthesized by simple and cost effective sol-gel process. The dried powders have been sintered at high temperatures from 200 °C to 800 °C for 2 hours in a conventional muffle furnace in air ambient. The visible photocatalytic property of the pure ZnS and CuS doped in ZnS have been tested for the degradation of standard dyes namely Methylene Blue, Methyl Orange, and Methyl Red along with chemical effluent. The samples have been characterized for their structural, chemical and morphological properties by employing X-ray Diffraction (XRD), Fourier Transform Infra-Red spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) techniques, respectively in order to understand the structure –property relationship.

2. Experimental Procedure

2.1. Materials

Zinc Nitrate dihydrate (ZnNO₃·2H₂O), copper chloride hexahydrate (CuCl₂·6H₂O), cetyltrimethylammonium bromide [(C₁₆H₃₃)N(CH₃)₃Br] (CTAB), Thiourea (SC(NH₂)₂) and Ammonia solution were procured from Merck chemicals, India. The chemicals used were of analytical grade and had a purity higher than 99 %. Dyes Methylene Blue, Methyl Red and Methyl Orange were purchased from Nice chemicals, India and were used for making dye solutions.

2.2. Synthesis of ZnS: CuS

Solutions of Zinc Nitrate (A), Copper Chloride (B), CTAB (C) and Thiourea (D) were prepared in 100 ml of ethanol as a solvent by taking calculated amount of each. A simple magnetic stirrer setup was used to stir until clear solutions were obtained. The copper chloride solution was added dropwise to the zinc nitrate solution and stirred till a clear solution was obtained (E). CTAB solution prepared was added to the mixture obtained previously to obtain the sol (F). The prepared Thiourea solution was added dropwise to the sol. The sol converts to a thick viscous gel (G). Calculated amount of Ammonia solution was added to the gel to precipitate the particles from the gel formed. The solution was then filtered using Whatman 42 filter paper. The particles obtained were dried in a hot air oven for 2 hours and then further sintered for 2 hours in a muffle furnace. The sintered sample was subjected to characterization for their structural and morphological properties by employing XRD, SEM and XPS techniques, respectively.

Nomenclature

A	Zinc Nitrate solution
B	Copper chloride solution
C	CTAB solution
D	Thiourea solution
E	Zinc Nitrate and copper chloride solution
F	Zinc Nitrate, copper chloride and CTAB solution – SOL
G	Zinc Nitrate, copper chloride, CTAB and Thiourea solution – GEL

3. Characterization

The sintered samples were characterized for their structural, elemental and morphological properties by employing X-ray Diffraction (XRD), X-Ray Photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM) techniques respectively in order to understand the structure –property relationship. XRD images were taken by using Bruker-eco D8 Advance for 2θ values ranging from 10° to 80° and a $\text{CuK}\alpha$ radiation of wavelength $1.5418 \text{ \AA}$ scanned at a rate of 1° per minute. SEM images were observed using Tescan VEGA 3 for three different resolutions. XPS images were taken using K-Alpha^{TM+} for binding energy ranging from 0 to 1000 eV.

4. Results and Discussion*4.1. Morphological studies using SEM images*

The surface morphology of ZnS: CuS was observed using SEM images. The size of the nanoparticles formed along with their shape can be determined by SEM analysis. The SEM images of ZnS: CuS taken at three different magnifications are shown in Fig. 1 (a, b and c).

4.2. X-Ray Diffraction analysis

The crystal structure of nano ZnS:CuS was determined by X-ray diffraction pattern. The XRD pattern for the ZnS: CuS sintered at 200°C is shown in Fig. 2. From the XRD analysis, sharp peaks at 2θ values of 28.65° , 47.78° , 56.45° , 69.86° and 77.38° were observed corresponding to Miller indices (111), (220), (311), (400) and (331), respectively. The sample has cubic structure of ZnS with lattice parameters $a = b = c = 5.3903 \text{ \AA}$. Lattice parameters calculated are within the error range obtained from standard literature value where $a = 5.406 \text{ \AA}$ from JCPDS standard card 00-005-0566.

The crystalline size of the prepared ZnS: CuS was calculated using Debye-Scherrer's equation [14] as shown in Eq. (1)

$$D = 0.9\lambda/\beta \cos \theta \quad (1)$$

Where D is crystalline size

λ is the wavelength of X ray

β is Full-Width Half Maximum of (FWHM) of the peak

θ is the angle of diffraction

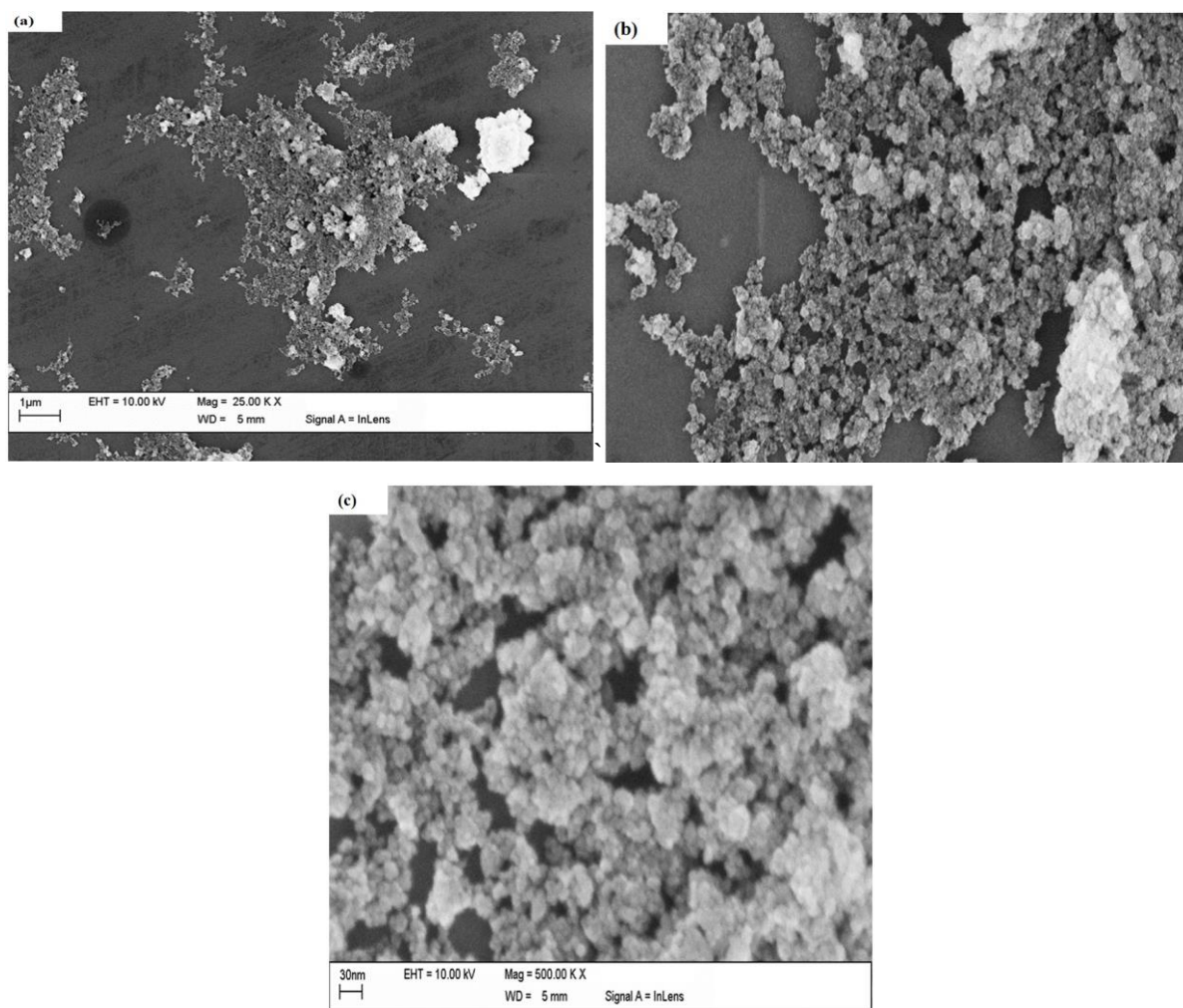


Figure. 1. SEM Images of ZnS doped with CuS sintered at 200 °C for 2 hours (a) Low magnification (scale bar: 3 microns) (b) High Magnification (Scale bar: 200nm) and (c) High magnification (Scale bar 30nm).

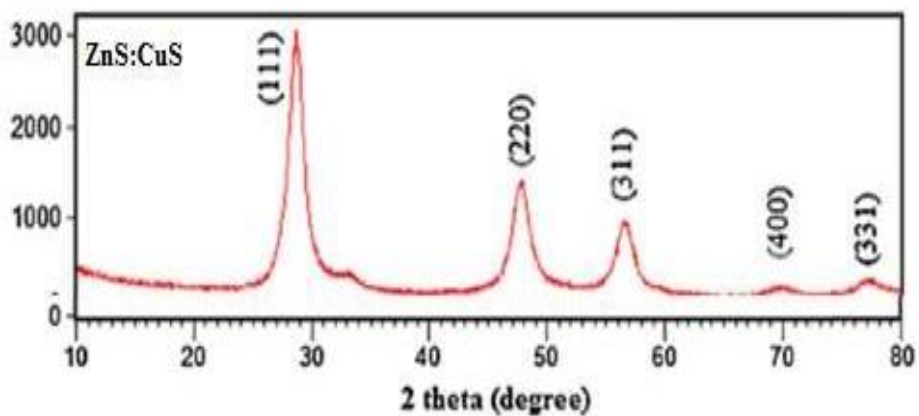


Figure. 2. X-ray diffraction pattern for synthesized nano-ZnS: CuS sintered at 200 °C for 2 hours

4.3. X-ray photoelectron spectroscopy (XPS) studies

The elemental composition of the synthesized nano-ZnS: CuS was obtained by XPS analysis. Fig. 3(a and b) shows the X-ray photoelectron spectroscopy for the synthesized sample. In the general survey spectrum, it was observed that the main component of the material ZnS along with dopant concentration copper. Peaks for carbon and oxygen were also observed at 535 eV and 284 eV, respectively. In order to check the copper concentration in the sample core level binding energy calculations have been measured where we could see Cu 2p is splitting into Cu 2p_{3/2} and Cu 2p_{1/2}. No impurity peaks have been observed other than the main component. Cu Auger LMM peak has also been observed which has been depicted in the inset of copper core level spectra.

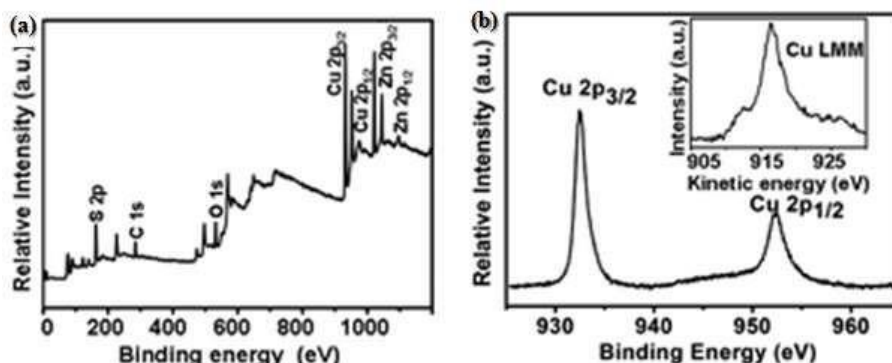


Figure.3. X-ray photoelectron spectroscopy pattern for synthesized nano-ZnS: CuS sintered at 200 °C for 2 hours

4.4. Photocatalytic Activity

The dye solution was prepared by adding 0.01 g/l of Methylene Blue dye (purchased from NICE Chemicals) in a 1lt volumetric flask. Double distilled water was used to make the solution. The prepared solution was tested for its absorbance using a UV-Vis Spectrophotometer. The peak for Methylene Blue solution was observed at 667 nm with a small shoulder at 621 nm. About 100 ml of the dye solution was transferred to a 250 ml beaker on a magnetic stirrer setup. Above the beaker, a 100 W bulb was hung using simple stand support which was the source of the visible light. About 100 mg of the ZnS: CuS sintered at 200 °C was added at once to the dye solution immediately after weighing. Stirring was started and rpm was set to a steady constant value and simultaneously stop clock was started. After 10 minutes, the stirring was stopped, after giving adequate time for settling of the particles, about 5ml of the solution was drawn using a syringe without disturbing the settled particles. The solution was drawn in every 10-minute interval and tested for absorbance. From the absorbance versus wavelength (nm) graph as shown in Fig. 4, it was observed that at 667 nm the peak was gradually decreasing and it was negligible after 30 minutes. Though there was no peak there was a shift in the absorbance curve for the treated samples.

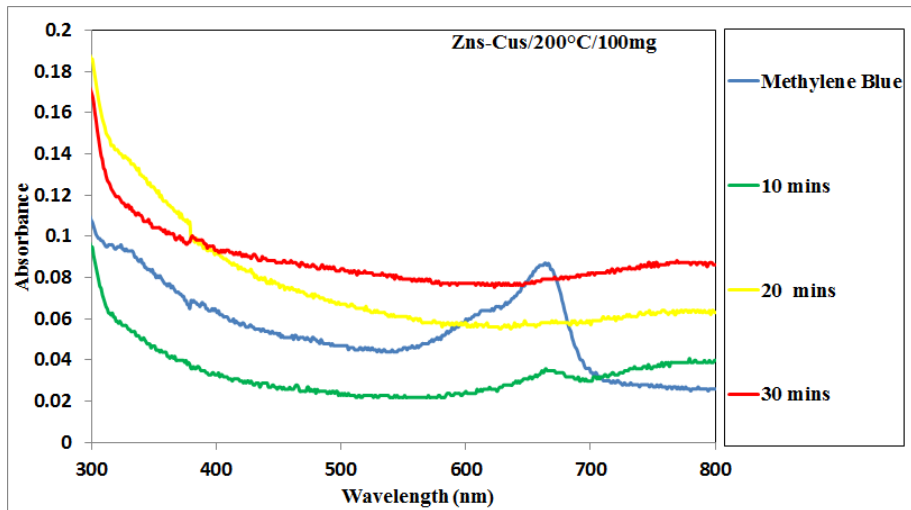


Figure. 4. Degradation of Methylene Blue dye (conc.0.01 g/l) with 100 mg of ZnS: CuS sample sintered at 200 °C for 2 hours.

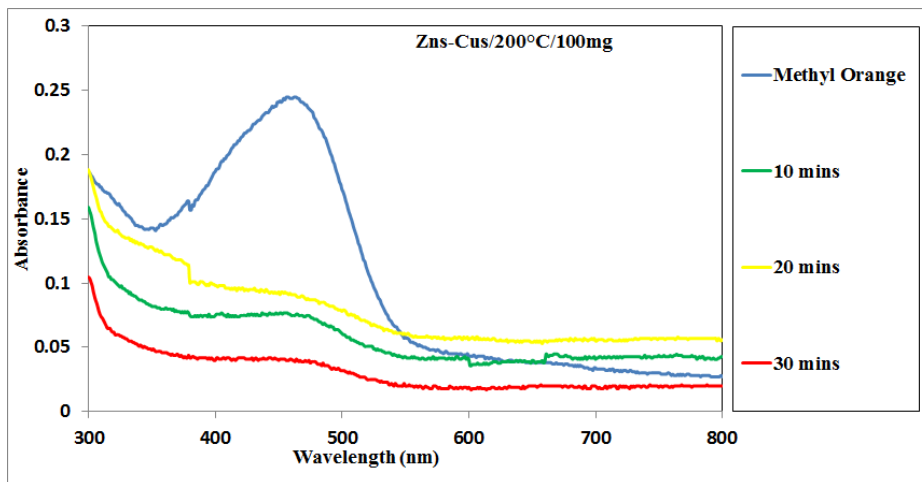


Figure.5. Degradation of Methyl Orange dye (conc.0.01 g/l) with 100 mg of ZnS: CuS sample sintered at 200 °C for 2 hours

In addition to testing Methylene Blue, the sample was tested on Methyl Orange and Methyl Red solutions. The prepared Methyl Orange and Methyl Red solutions were tested for their absorbance using a UV-Vis Spectrophotometer. The peaks were observed at 464 nm and 433 nm for Methyl Orange and Methyl Red solutions respectively. From the absorbance versus wavelength (nm) graphs for Methyl Orange, as shown in Fig. 5, it can be observed that at 464 nm the peak was gradually decreasing and it was negligible after 30 minutes.

From the absorbance versus wavelength (nm) graphs for Methyl Red, as shown in Fig. 6, it can be observed that at 433 nm the peak was gradually decreasing and it was negligible after 30 minutes.

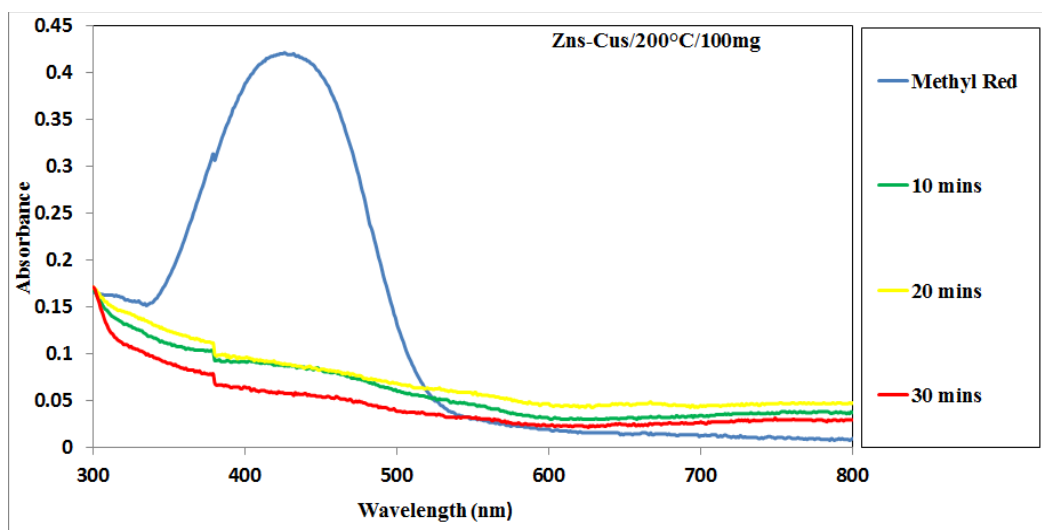


Figure. 6. Degradation of Methyl Red dye (conc. 0.01 g/l) with 100 mg of ZnS: CuS sample sintered at 200 °C for 2 hours

Similar degradation was attempted on 100 ml of the dye solution and 100 mg of the sample without the bulb and sun as a source of light. From the absorbance versus wavelength (nm) graph as shown in Fig. 7, it was observed that at 433 nm the peak had significantly reduced after 30 minutes. But, it can be seen that with Sun as a source, the degradation is 30 % less as compared to that with the bulb as a light source. Since the source of light from the sun is not focused directly on the system, the degradation is limited.

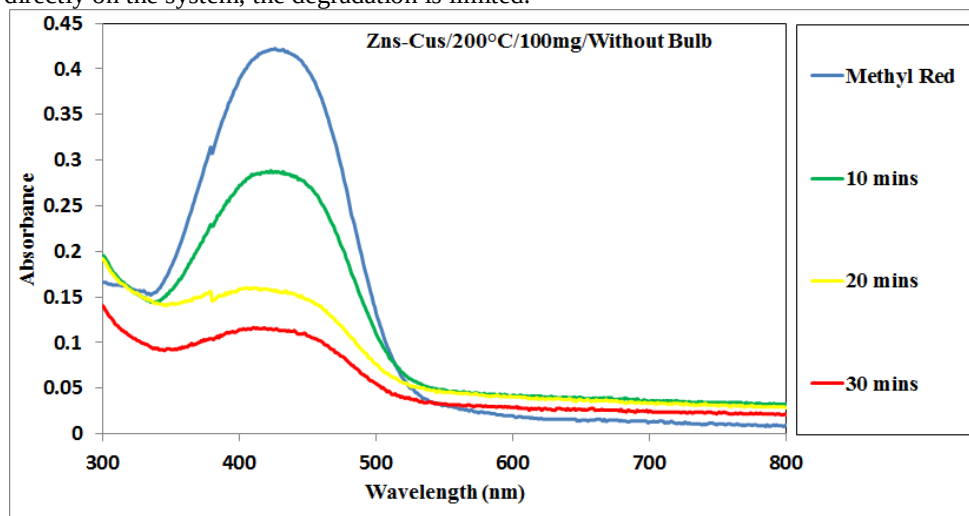


Figure. 7. Degradation of Methyl Red dye (conc. 0.01 g/l) with 100 mg of ZnS: CuS sample sintered at 200 °C for 2 hours under sunlight.

To check the reusability of the photocatalytic material, the used sample was filtered, dried in a hot air oven for 2 hours and was used for degrading a fresh dye solution. From the absorbance versus wavelength (nm) graph as shown in Fig. 8, it can be observed that at 433 nm the peak had reduced and the degradation was 60 % of what was obtained with the fresh sample, after 30 minutes.

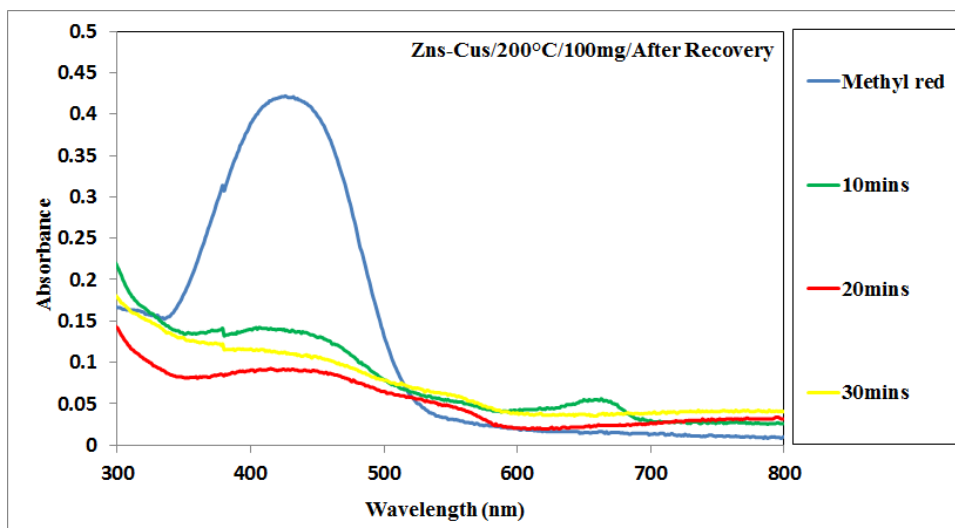


Figure. 8. Degradation of Methyl Red dye (conc.0.01g/l) with 100 mg of ZnS: CuS sample sintered at 200°C for 2 hours recovered and tested

After degrading dye solution with 100 mg of ZnS: CuS, similar tests were conducted with reduced quantity of photocatalyst. About 50 mg of the ZnS: CuS sintered at 200 °C was added at once to the dye solution immediately after weighing. Stirring was started and rpm was set to a steady constant value simultaneously, stop clock was started. After 10 minutes, the stirring was stopped and after giving adequate time for settling of the particles, 5 ml of the solution was drawn using a syringe without disturbing the settled particles. The solution was drawn in every 10-minute interval and tested for absorbance. From the absorbance versus wavelength (nm) graph as shown in Fig. 9, it can be observed that at 667nm the peak was gradually decreasing and it was negligible after 30 minutes. A shift in the absorbance was also observed.

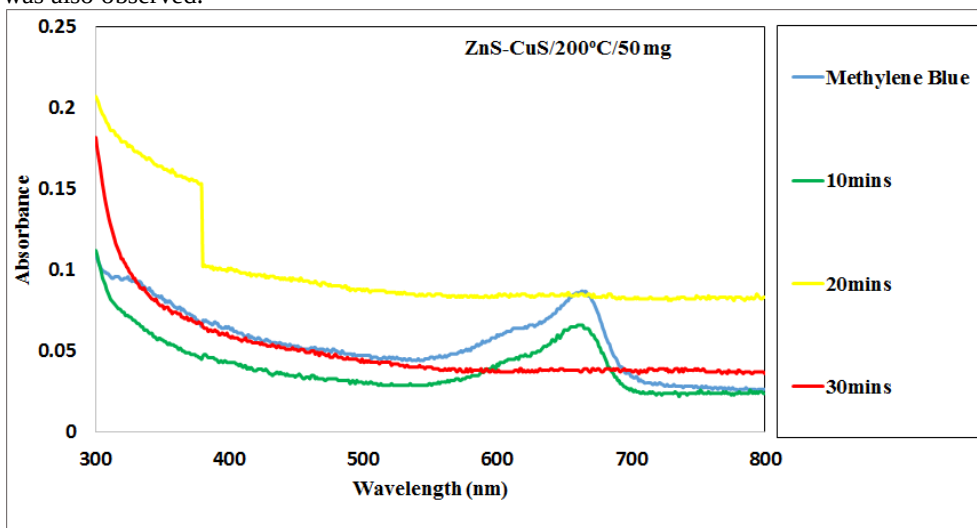


Figure. 9. Degradation of Methylene Blue dye (conc.0.01 g/l) with 50 mg of ZnS: CuS sample sintered at 200 °C for 2 hours

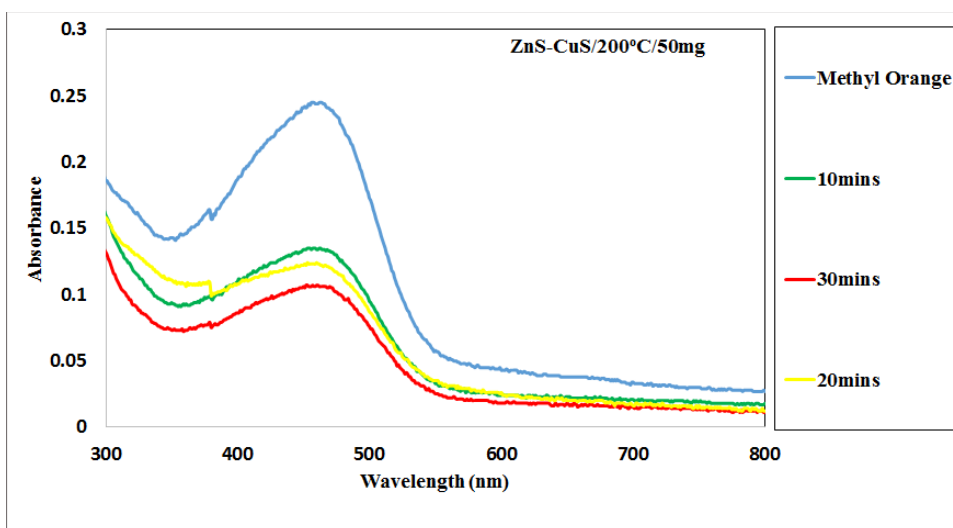


Figure. 10. Degradation of Methyl Orange dye (conc.0.01 g/l) with 50 mg of ZnS: CuS sample sintered at 200 °C for 2 hours

A similar degradation was observed on 100 ml of Methyl Orange dye solution and 50 mg of the sample. From the absorbance versus wavelength (nm) graph as shown in Fig. 10, it can be observed that at 467 nm the peak had partially reduced after 30 minutes.

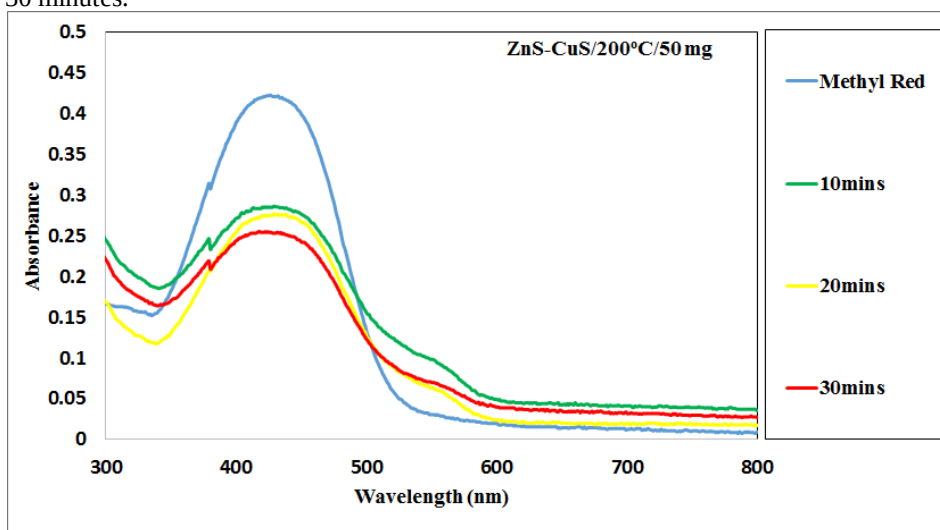


Figure. 11. Degradation of Methyl Red dye (conc.0.01 g/l) with 50 mg of ZnS: CuS sample sintered at 200 °C for 2 hours

Similar degradation experiment was performed on 100 ml of Methyl Red dye solution and 50 mg of sample. From the absorbance versus wavelength (nm) graph as shown in Fig. 11, it can be observed that at 433 nm the peak had partially reduced after 30 minutes.

The material was used to degrade a pharma effluent. From the absorbance versus wavelength (nm) graph as shown in Fig. 12, it can be observed that at 269 nm there was only a slight reduction in peak after 30 minutes and the peak was observed in UV region.

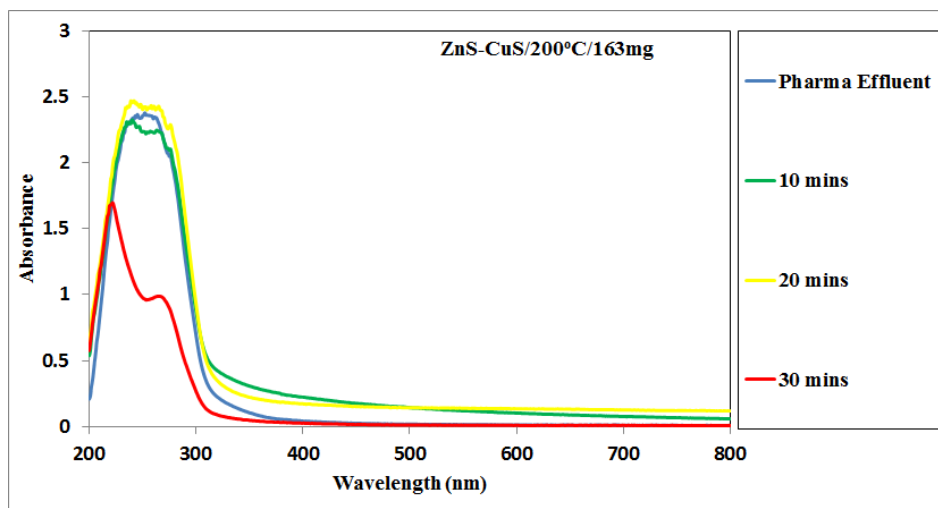


Figure. 12. Degradation of pharma effluent (conc.0.01 g/l) with 100 mg of ZnS:CuS sample sintered at 200 °C for 2hours

5. Conclusion

The sample sintered at 200 °C has shown nanostructure morphology with size as low as 25 nm to 100 nm as shown in the high magnification of the SEM image. ZnS: CuS sample sintered at 200 °C for 2 h in ambient air has shown a simple cubic structure similar to that of ZnS with no indication of CuS (as the additive is below 5%). ZnS: CuS sample sintered at 200 °C has been measured for elemental analysis by X-Ray Photoelectron Spectroscopy where it is clearly identified that Cu is present in very small quantity.

It can be concluded from this work that the ZnS: CuS sample could successfully degrade the dye solutions in 30 minutes and the material is reusable with lower degradation efficiency which is due to the inefficient method of catalyst recovery. The material has a very good potential to be used in textile industry for reducing the colored effluent released by the industry. The material also does not seem to show the same degradation ability on pharma effluent. Further work is being carried out to optimize the copper doping, the amount of catalyst required for degradation and the time required for degradation. Also, an efficient method of material recovery is required for increasing the amount of catalyst recovered.

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