# Morphological studies and photocatalytic degradation of methylene blue by zinc sulfide nanoparticles

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We report the preparation, morphological and photocatalytic studies of zinc sulfide nanoparticles from zinc(II) dithiocarbamate precursors. Powder X-ray diffraction patterns were index to the wurtzite crystalline phase of zinc sulfide while transmission electron microscopy micrographs revealed spherically shaped particles with sizes in the range 2.8 to 5.2 nm. The ZnS nanoparticles were used as photocatalysts for the degradation of methylene blue with degradation efficiency of 71.41% for ZnS1 and 85.95% for ZnS2 nanoparticles at pH 9.43. The effect of catalyst concentration, pH, radical scavengers, and hole ( $h^+$ ) scavengers on the photodegradation of methylene blue dye were evaluated.

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## 1. Introduction

Dithiocarbamates are of interest among metal chalcogenides due to their use as single source precursors for the preparation of semiconductor metal sulfide nanoparticles due to their stability and good thermal decomposition properties [1]. As the diameter of nanoparticles approaches their Bohr diameter, it generates size dependent optical and electronic properties that is significantly different from those of bulk materials [2-3]. These unique properties are largely associated with the physical characteristics such as diameter, molar volume, morphology and dispersibility of the nanoparticles [4]. Among semiconductor nanoparticles, transition metal chalcogenides are of interest because some can exist in different stoichiometric that leads to variable optical band gaps [5]. Semiconductors with narrow-band gap possess enhanced photocatalytic activities in comparison with bulk materials [6]. Zinc sulfide semiconductors materials are of interest due to their potential applications for optoelectronics devices [7-8], solar cells [9], sensors [10] and as photocatalyst [11-12]. It is regarded as one of the most important ntype semiconductor metal chalcogenides with band gap that varies from 3.66 eV for cubic phases to 3.9 eV for hexagonal crystalline phases [13-15]. The band gaps of ZnS nanoparticles are of interest in photocatalysis due to their high energy change efficiency [16]. It has been reported that ZnS nanoparticles prepared from single source precursors are photo catalytically active [17]. The photocatalytic activity of semiconductors nanoparticles depends on their crystalline phase, surface area, particle size, band gap energy and morphology [18]. The particle sizes of metal sulfide nanoparticles can be influenced by variation in reaction temperature, time, precursor, and capping agents [19]. In this study, we report the use of bis(N-methylbenzyldithiocarbamato)Zn(II) and bis(2,3-dimethylbenzyldithiocabamato)Zn(II) complexes as precursors to prepare ZnS nanoparticles. The complexes were thermolyzed at 180 °C to study the effect of precursors on the structural and optical properties of the as-prepared ZnS nanoparticles. The effect of catalyst concentration, pH,  $\cdot$ OH radical and hole (h<sup>+</sup>) scavengers on photodegradation of methylene blue dye by the as-prepared ZnS nanoparticle were investigated.

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## 2. Materials and methods

#### 2.1. Materials

All reagents were of analytical grade and used without further purification. N-methyl dithiocarbamate, 2,3-dimethyl dithiocarbamate and their corresponding zinc(II) complexes were prepared using modified literature procedure [20,21].

## 2.2. Synthesis of oleylamine capped ZnS Nanoparticles

Suspension of bis(N-methylbenzyldithiocarbamato)Zn(II) in tri-octylphosphine (TOP) was injected into hot 10 mL oleylamine at 180 °C. The mixture was stirred continuously for 1 h, thereafter the resultant solution was left to cool to 70 °C. Cold methanol was added, and the asprepared ZnS nanoparticles were collected by centrifugation at 5000 rpm for 30 min. The resultant product was labelled ZnS1. The synthetic process was repeated using bis(2,3-dimethylbenzyldithiocarbamato)Zn(II) and the as-prepared zinc sulfide nanoparticles labelled ZnS2.

## 2.3. Characterization of oleylamine capped ZnS Nanoparticles

The ZnS nanoparticles particle sizes were obtained using transmission electron microscope (TEM) JEOL 1600. The morphology and elemental composition were studied by scanning electron microscope (SEM) ZEISS FEGSEM attached with energy dispersive X-ray (EDX) analyzer. The phase and structure determination were carried out using Bruker D8 advance powder X-ray diffractometer with CuK $\alpha$  ( $\lambda = 1.5405$  Å) radiation. Perkin-Elmer Lambda 25 UV-visible spectrophotometer was used to record absorption spectra of the prepared ZnS nanoparticles at room temperature. Photoluminescence spectra are recorded by Perkin-Elmer LS 45 fluorescence spectrophotometer.

#### 2.4. Photocatalytic reactions

The photodegradation of methylene blue was study in the presence of the as-prepared ZnS nanoparticles (catalyst) under high-pressure mercury vapour lamp (70W) as a visible light irradiator. The catalyst (5 mg) was placed in seven vials containing 5 mL of methylene blue (10 ppm). The solution was stirred for 30 min in the dark to attain adsorption/desorption equilibrium of the dye on the catalyst. All the vials containing the reactants were stirred using magnetic stirrer to ensure uniform suspension of the catalyst during the reaction. To determine the degradation of methylene blue, the vials were collected at regular intervals (30 min) for 3 h. The samples were centrifuged to remove the nanoparticles. The concentration of the dye was measured at  $\lambda_{max}$  of 664 nm by UV-vis spectrometry. The degradation efficiency (%) was calculated using equation (2).

Degradation efficiency (%) = 100 × 
$$\left[\frac{(C_0 - C_t)}{C_0}\right]$$
 (2)

where, " $C_0$ " is the initial concentration of the dye, " $C_t$ " is the concentration of dye at time t, and "t" is the time of sample irradiation.

To detect the reactive oxidative species responsible for the degradation process, isopropanol and potassium iodide was used as  $\cdot OH^-$  (hydroxy radical) and h<sup>+</sup> (holes) scavengers. To study the effect of pH on the photodegradation process, the initial dye solution was adjusted with 0.1 M HCl or 0.1 M NaOH.

### 3. Results and discussions

#### 3.1. Morphological studies

The powder X-ray diffraction patterns of the ZnS nanoparticles (Figure 1) revealed diffraction peaks at 22.89°, 25.65°, 27.60°, 33.47°, 55.77°, and 66.70° corresponding to (002), (100), (101), (111), (200), (220), (112), and (400) planes of wurtzite ZnS crystalline phase for

ZnS1 while the XRD patterns for ZnS2 nanoparticles showed peaks at  $23.47^{\circ}$ ,  $27.71^{\circ}$ ,  $33.47^{\circ}$ ,  $47.14^{\circ}$ ,  $55.88^{\circ}$  and  $66.82^{\circ}$  corresponding to (002), (101), (111), (200), (220), (110), (112) and (400) planes. These are characteristic peaks of ZnS corresponding to the wurtzite structure of ZnS nanoparticles. The peaks were indexed to those reported in the JCPDS card no. 36-1450 [22-24].



Fig. 1. p-XRD pattern of oleylamine-capped ZnS nanoparticles.

Transmission electron microscopy micrographs of the as-prepared ZnS nanoparticles (Figure 2) revealed monodisperse spherically shaped particle for ZnS1 prepared from bis(N-methylbenzyldithiocarbamato)Zn(II). The particles sizes of the as-prepared ZnS1 ranges from 4.33-5.22 nm. ZnS2 prepared from bis(2,3- dimethylbenzyldithiocabamato)Zn(II) are spherical in shape and monodisperse with particle sizes in the range 2.80-3.50 nm. ZnS2 are smaller in sizes in comparison to ZnS1 and very few particles of ZnS2 were obtained which indicates that bis(N-methylbenzyldithiocarbamato)Zn(II) is better single source precursor for the preparation of ZnS nanoparticles than bis(2,3- dimethylbenzyldithiocabamato)Zn(II).



Fig. 2. TEM images and size distribution graph (insert) for oleylamine-capped ZnS nanoparticles.

SEM was used to investigate morphology and EDS was used to determine the elemental compositions of the as-prepared ZnS nanoparticles. SEM images for both ZnS nanoparticles showed smooth surface in Figure 3, while EDS spectra showed the presence of zinc and sulfur atoms, confirming the formation of ZnS nanoparticles.



Fig. 3. SEM images and corresponding EDX spectra for oleylamine-capped ZnS nanoparticles.

## 2.2. Optical properties of the oleylamine-capped ZnS nanoparticles

The UV-Vis absorption spectra of oleylamine-capped ZnS nanoparticles are shown in Figure 4a below. A strong absorption peak is observed at 207 and 217 nm for ZnS1 and ZnS2 nanoparticles, respectively. The peaks suggest a blue shift in the absorption band edges in comparison to that of bulk ZnS (354 nm). These peaks are due to electron transitions from valence band to conduction band which indicates the as-prepared ZnS nanoparticles could be used as photocatalysts. The energy band gap of the ZnS nanoparticles were calculated using Tauc plots with estimated band gaps of 4.10 and 4.41 eV for ZnS1 and ZnS2 nanoparticles. The band gaps showed considerable blue shift from that of bulk ZnS (3.65 eV). The photoluminescence spectra of the ZnS nanoparticles under excitation of 350 nm was used to investigate surface vacancies, transfer, and recombination of photo- generated electron-hole pairs on the nanoparticles are shown in Figure 4b. The emission maxima at 442 and 420 nm for ZnS1 and ZnS2 could be attributed to the release of trapped luminescent particles [25], recombination of interstitial sulfur, or interstitial zinc and sulfur vacancies [26,27].



Fig. 4. Absorption (a) and photoluminescence (b) spectra of oleylamine-capped ZnS Nanoparticles.

# 3.3. Photocatalytic degradation of methlene blue of oleylamine-capped ZnS nanoparticles

The photocatalytic activity of the ZnS nanoparticles was studied using photocatalytic degradation of methylene blue dye at different irradiation times. Electronic absorption spectroscopy was used to evaluate the photodegradation as presented in Figures 5a and 5b. The photodegradation efficiency of methylene blue by ZnS1 and ZnS2 nanoparticles are 55.97 and 65.92%, respectively (Figure 4c). ZnS2 showed higher degradation efficiency with a rate constant of 0.00594 min<sup>-1</sup>. The higher degradation observed by ZnS2 could be attributed to the larger band gap energy of 4.41 eV as well as the monodispersity of the as-prepared ZnS1. Upon light irradiation, electrons are promoted from the valence band to conduction band causing generation of holes and radicals responsible for the photodegradation of methylene blue dye. The morphology of the ZnS1 nanoparticles may have played a part in the photocatalytic activity of the ZnS1 and ZnS2 nanoparticles.



Fig. 5. The degradation of MB by oleylamine-capped ZnS nanoparticles: UV-visible spectra (a,b) degradation efficiency (c) and kinetics plot (d).

The effect of oleylamine-capped ZnS as photocatalysts for the degradation of methylene blue dyes was studied by varying the concentration from 1 mg to 5 mg at a constant dye concentration (10 ppm). The photocatalyst dosage degradation efficiency as shown in Figure 6 shows a significant increase in degradation efficiency as the concentration is increased from 1 mg to 5 mg. ZnS1 showed degradation efficiency of 50.94% for 1 mg, 55.97% for 3 mg and 62.97% for 5 mg, the same trend was observed in ZnS2. The increase in photodegradation efficiency could be ascribed to the availability of effective site on the photocatalyst surface as the catalytic dosage increases. However, it has been reported that higher concentration reduces degradation due to increase in suspension turbidity which hinders the penetration of light [28,29]. Hence, we adapted the use of 5 mg of catalyst in this study.



Fig. 6. Percentage degradation of MB dye at different concentration of oleylamine-capped ZnS nanoparticles.

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## 3.3.1. Effect of pH on the photocatalytic degradation of methylene blue

The role of pH is important in photocatalytic process as pH influences valence band oxidation potential [30], adsorption and dissociation of the dye functional group on the photocatalyst surface [31] and surface charge of the catalyst [32]. The photodegradation efficiency was evaluated in acidic (pH 3.17) and basic media (pH 9.43) using 0.1 M HCl and 0.1 M NaOH. ZnS1 nanoparticles was highly effective to photodegrade methylene blue in basic medium with degradation efficiency of 71.41% at pH 9.43 but only 7.31% of the dye was degraded at pH 3.17. The photodegradation efficiency of methylene blue dye by ZnS2 was 15.59% at pH 3.17 and 85.95% at pH 9.43 (Figure 6).



Fig. 7. Effect of pH on MB dye degradation by oleylamine-capped ZnS nanoparticles.

The photocatalytic degradation efficiency of the as-prepared ZnS nanoparticles increase with increase in pH with the highest degradation efficiency obtained at pH 9.43. At higher pH, COOH dissociates to form COO<sup>-</sup> which interacts with the positive surface of ZnS nanoparticles to increase the photocatalytic degradation efficiency [33]. The lower degradation efficiency obtained at pH 3.17 could be ascribed to the electrostatic repulsion between the methylene blue and highly accessible protons at lower pH values [33]. This ionic repulsion is due to the positively charged ZnS surface and the cationic methylene blue [34].

## 2.3.2. Effect of scavenging activity on the photocatalytic degradation of methylene blue

To understand the involvement of active species ( $h^+$  or •OH) in the photocatalytic degradation, scavengers were introduced under visible light irradiation to evaluate their influence on the photocatalytic degradation process. The reactive species ( $h^+$  or •OH) are important oxidizing agents that are involved in the photocatalytic process for the breakdown of the dye molecules to smaller products. To evaluate the reactive species contributions, potassium iodide and isopropanol were used as scavengers to trap  $h^+$  and •OH radicals, respectively.



Fig. 8. Effect of scavengers on MB dye photodegradation by oleylamine-capped ZnS nanoparticles.

In the presence of potassium iodide, the change in photodegradation efficiency is negligible. However, when isopropanol was added, the photodegradation efficiency reduced to 35.58% and 44.65% for ZnS1 and ZnS2, respectively. Therefore, OH is a dominant reactive species that took part in the photodegradation of methylene blue over oleylamine-capped ZnS nanoparticles. As a result of hydroxyl radical scavenging, there is a possibility that the rate of reaction will increase due to reduction of electron-hole pair recombination [35,36].

## 4. Conclusions

We present the morphological, optical, and photocatalytic degradation of methylene blue dye by ZnS nanoparticles prepared by thermal decomposition of bis(Nmethylbenzyldithiocarbamato)Zn(II) (ZnS1) and bis(2,3-dimethyldibenzyldithiocarbamato)Zn(II) (ZnS2). Powder X-ray diffraction patterns of the as-prepared ZnS nanoparticles confirmed wurtzite ZnS crystalline phase irrespective of the single-source precursors. TEM images revealed monodispersed ZnS nanoparticles with particle sizes in the range of 2.8 nm to 5.2 nm. Optical bandgap energy of 4.10 eV and 4.41 eV were obtained for ZnS1 and ZnS2 respectively which is blue shifted in comparison to bulk ZnS (3.65 eV). This could be attributed to quantum confinement due to the small particle size of the ZnS nanoparticles. The effect of ZnS catalysts dosage were investigated and optimum dosage of 5 mg at pH of 6 was used to evaluate the photocatalytic degradation of methylene blue by the as-prepared ZnS nanoparticles. The effect of pH on the photocatalytic degradation of methylene blue indicates basic medium is the best condition for the photocatalytic process. In addition, the role of photoactive species in the photocatalytic process was studied using radical scavenger techniques. The results shows that ZnS1 photo catalytically degraded 55.97% of methylene blue while 65.92% of methylene blue were degraded by ZnS2 nanoparticles

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