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Catalytic removal of methylene blue with different stoichiometric ratios of ZnCuS nanoparticles

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Abstract: Photocatalytic decomposition of methylene blue (BM) solution by Cu-doped ZnS nanoparticles in the presence of UV light has been studied. The effect of the molar ratio of Cu ions affecting the rate of degradation reaction has been investigated. Photocatalytic reactivity of ZnS:Cu nanoparticles could be tailored by the proper amount of Cu ions. The maximum decolorizing efficiency (85%) of 5 ppm MB was obtained by 30 mgL^{-1} nanoparticles containing 2 wt% Cu, which was ascribed to the most effective surface area of these particles. However, at more than 2 wt% Cu doping concentration, nanoparticles aggregated due to their high surface energy, and the decomposition efficiency was decreased.

Keywords: degradation percentage; dye methylene blue; photocatalysis; ZnS:Cu nanoparticles.

1 Introduction

One of the serious problems which threatens the health of humans, plants and animals is water pollution.

Water pollution is caused when effluents of industries are discharged into water sources without any treatment for the removal of harmful or dangerous compounds.

Different methods have been developed by researchers to wastewater treatment such as adsorbents [1], electrolyte decomposition, ion exchange method, biological methods, etc. [2–4]. These methods are not applicable at large scale due to high costs; therefore, some alternative methods are required. Using a photocatalyst is a reliable method which provides an ecofriendly pathway for the degradation of many organic pollutants [5]. This method is considered as a promising and green chemical procedure for wastewater treatment [6].

Photocatalyst can promote reactions in the presence of light and are not consumed in the overall reactions. For example, zinc sulfide (ZnS) is proven to be dynamic photocatalysts [7–9].

ZnS has remarkable properties among all the metal sulfides and it is one of the most widely investigated photocatalysts because it rapidly generates electron–hole pairs (excitons) under photoexcitation [10].

ZnS is II–VI compound semiconductor with direct and wide band gap (3.72 eV for the cubic zinc blende phase and 3.77 eV for the hexagonal wurtzite phase at room temperature) and a large exciton binding energy (40 meV), and therefore it can work only under ultraviolet (UV) light irradiation. ZnS has also exceptional stability against oxidation and hydrolysis. It has been widely used in light-emitting diodes, electroluminescence, chemical sensors, lasers, biosensors and solar cells [11–13].

ZnS has two kinds of structures: zinc blende (cubic crystal) and wurtzite (hexahedron) [14]. On the other hand, ZnS and ZnS doped by noble metals (Cu, Ag, Au and Co) have important environmental applications in wastewater treatment as an effective photocatalyst [15].

To improve the photocatalytic activity of materials, that is, increasing the interfacial charge transfer and decreasing the electron–hole recombination, their properties should be modified [16].

An effective way to do this is the doping of metals and nonmetals [17]. A dopant ion may act as an electron trap or hole trap. This would prolong the life time of the charge carriers, resulting in an enhancement in photocatalytic properties [18].

When a noble metal is doped into a wide band gap semiconductor, an intermediate band (IB) energy level is introduced in between the valence and conduction bands. Therefore, the band gap of semiconductor is reduced. Under illumination, this leads the electrons in semiconductor to move from valence band to conduction through IB levels that it generates charge carriers (electrons and holes) [19, 20].These holes lead to a form of hydroxyl radicals (•OH) which are responsible for degradation. The ionic radius of Cu^{2+} is 73 pm, while the ionic radius of Zn^{2+} is 74 pm, then

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introduction of Cu ions into the ZnS phase reduces the band gap in this structure.

As a result, the role of doped noble metal is creating and transferring of charge carriers in the presence of light. Therefore, increasing the available surface area of photocatalyst leads to increase in degradation efficiency [21].

An intermediate band (IB) is created by the energy levels of bound states of dopants (Cu ions) within the band gap of host semiconductor (ZnS) that acts as an electron (or hole) trap to transfer electrons (or holes) from the valence band (VB) to the conduction band (CB) via the absorption of two subband gap photons (hν). The most important aim of the present work is optimizing the water treatment methods by the photocatalytic removal of methylene blue with ZnCuS nanoparticles.

2 Experimental procedure

2.1 Synthesis of ZnS:Cu nanoparticles

All starting raw materials including zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, purity 97%), sodium sulfide ($Na_2S{\cdot}9H_2O$, purity 98%), copper acetate ($Cu(CH_3COO)_2{\cdot}H_2O$, purity 97%) and polyethylene glycol 6000 (PEG, purity 98%) were purchased from Sigma-Aldrich Chemical Co. All chemicals and solvents were used without further purification or treatment.

Pure and copper-doped ZnS nanoparticle crystals were prepared by co-precipitation reaction using $Zn(CH_3COO)_2{\cdot}2H_2O$, $Na_2S{\cdot}9H_2O$, $Cu(CH3COO)_2{\cdot}H_2O$ and PEG as source materials. PEG acted as the capping agent and the deionized water was used as a solvent.

Transmission electron microscopy (TEM) images were taken with a TESCAN MIRA3 and JEM-2010 UHR, 200 kV electron microscopes, respectively. The structural characterization of nanoparticles was measured by Philips (X'Pert Pro MPD) X-ray diffractometer with (40 kV and 40 mA) Cu-Kα radiations (λ = 1.5404 Å) in 2θ range from 20° to 80°. The optical properties were characterized by performing transmission measurements using Perkin.

The ZnS:Cu nanoparticle crystals were prepared in the following successive procedures: A 0.1 M zinc acetate, and PEG were dissolved in 50 mL of deionized water under continuous stirring. Then, the copper acetate with different concentrations (wt% in Zn = 0.5, 1, 2, 5 and 10%) was added to this premade solution. Finally, a 0.1 M sodium sulfide was dropwise added into the solution. After the reaction was completed, a white precipitate formed. Then the production was centrifuged at 3000 rpm for 2 min and dried at 200 °C for 12 h in air. By this way, samples ZnS, $Zn_{0.995}Cu_{0.005}S$, $Zn_{0.99}Cu_{0.01}S$, $Zn_{0.98}Cu_{0.02}S$, $Zn_{0.95}Cu_{0.05}S$ and $Zn_{0.9}Cu_{0.1}S$.

3 Results and discussion

Figure 1 shows the XRD patterns of ZnS:Cu nanoparticles prepared using different concentrations of Cu and Zn. It could be seen that three main diffraction peaks (111), (220) and (311), at 2θ = 28.6°, 48° and 56.8° are matched with the cubic structure of ZnS (JCPDS 05–0566, a = 0.5406 nm) [22, 23]. The XRD patterns also confirm the preferred orientation along (111) plane.

It could be seen that by increasing the Cu-doping ratio, the (111) peak becomes stronger and no significant change in diffraction angles with a noticeable increment in the intensity is observed. This could be attributed to the closer ionic radius of Zn^{2+} (0.74 Å) and Cu^{2+} (0.73 Å) [24]. No secondary phases such as Cu cluster and copper oxides are seen from XRD analysis. Since the intensity of the (111) peak remains almost stationary, the crystalline quality of ZnS nanoparticles doesn't alter significantly.

The grains of nanoparticles exhibit a regular round shape with a gibbous center. The transmission electron microscopy (TEM, LEO 906, Zeiss, Germany, 100 kV) analysis of the prepared ZnS:Cu nanoparticles in Figure 2

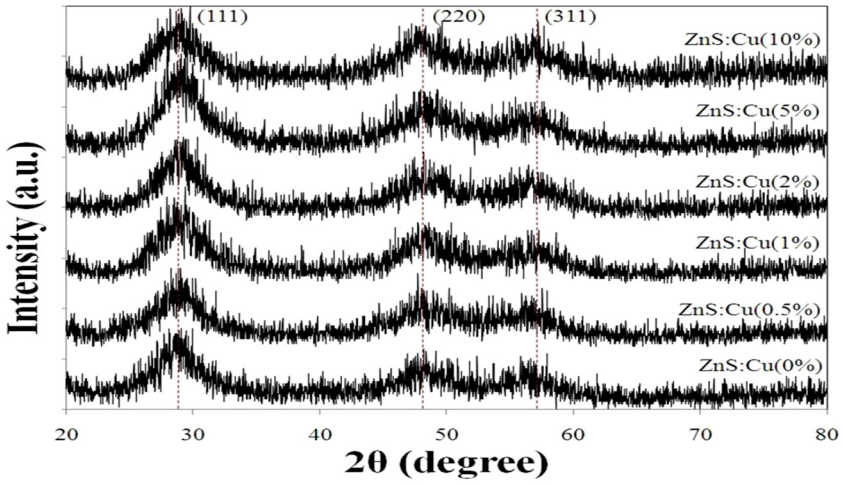

Figure 1: XRD patterns of ZnS:Cu nanoparticles with different concentrations of Cu and Zn prepared by Stober method.

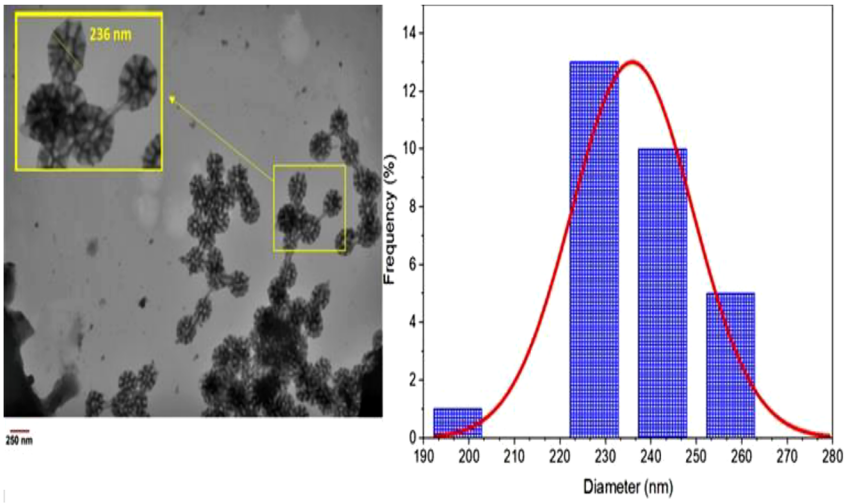

Figure 2: TEM image of the prepared Turtleback ZnS:Cu nanoparticles, data and the size of particles extracted from Digimizer software.

indicate that prepared samples could be noted as ultrafine nanocrystals with an average size of about 200 nm. The grains of nanoparticles exhibit Turtleback shapes, regular round shape with a gibbous center.

As the catalytic reaction is a surface phenomenon, the photocatalytic reaction is very sensitive to the surface structure of the material. In larger surface areas, more photocatalytic reactions take place. Therefore, the degradation of methylene blue solution was examined for ZnS:Cu films [22] and nanoparticles. In our previous work, the degradation of dye molecules by ZnS:Cu films was investigated. Results showed that a higher degradation efficiency of 56% could be obtained for a sample with ZnS:Cu (2%) in 360 min exposure time. In the present study, the photocatalytic activity of ZnS:Cu nanoparticles is studied.

For photocatalytic activity analysis, a UV lamp (Handheld PHILIPS 8W UVA Lamp) positioned above the beaker was used as a light source to cause the photocatalytic reaction.

The structure of methylene blue and schematic degradation mechanism of MB by pure ZnS and ZnS:Cu nanoparticles are shown in Figure 3.

The electrons and holes occupying the IB level, participate in the degradation of MB molecules. Therefore, more MB molecules could be degraded by ZnS:Cu photo catalysts compared with pure ZnS, as schematically shown in Figure 3(b).

The following scheme is proposed for the degradation of the methylene blue (MB) dye [25, 26]:

$$ZnS + h\vartheta \rightarrow ZnS^{*}\ (ZnS + e^{-}_{CB}\, h^{+}_{VB})$$

$$ZnS + H_2O \rightarrow ZnS^{*} + H^{+} + OH^{-}$$

$$h^{+}_{VB} + H_2O \rightarrow H^{+} + {}^{\circ}OH$$

$$e^{-}_{CB} + O_2 \rightarrow {}^{\circ}O^{-}_{2}$$

$$e^{-}_{CB} + h^{+}_{VB} \xrightarrow{\text{Recombination}} \text{heat}$$

$${}^{\circ}OH + \text{(MB)Dye} \xrightarrow{\text{Degradation}} CO_2 + H_2O + \text{MineralSalts}$$

In this study, a simple route is used for the preparation of undoped and Cu-doped ZnS nanoparticles ($Zn_{1-x}\,Cu_x\,S$; where x = 0.0, 0.5, 1.0, 2, 5 and 10), via the Stober method in ultrasound medium. The synthesis of copper-doped ZnS occurs according to the following reaction:

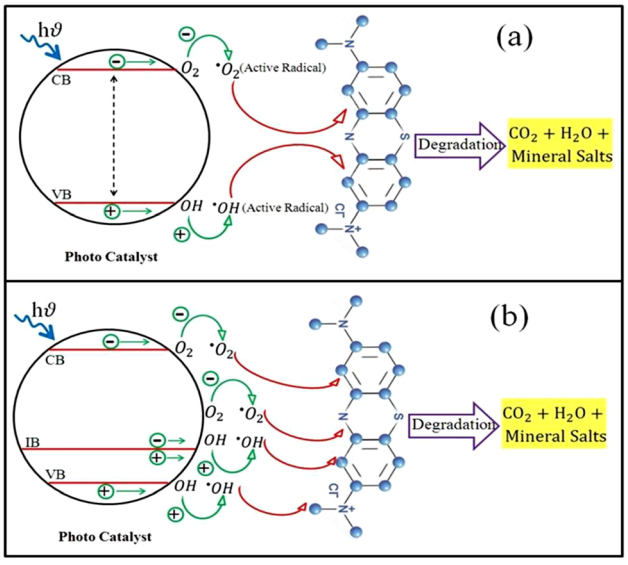

Figure 3: Representation of degradation of MB in (a) pure ZnS, (b) ZnS:Cu with intermediate band.

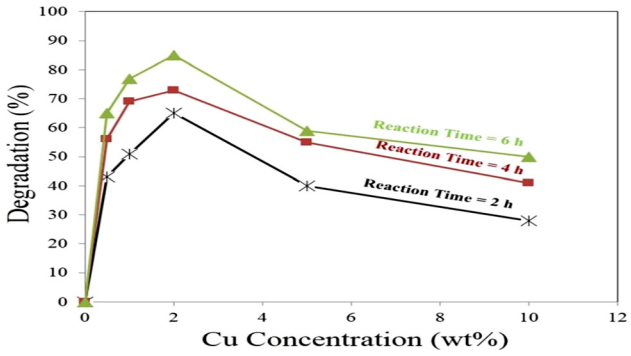

Figure 4: Degradation of MB with ZnS nanoparticles containing different concentrations of Cu for different reaction times of 2, 4 and 6 h 30 mgL^{-1} ZnS:Cu, [MB] = 5 ppm.

$$[Cu^{2+}/Zn^{2+}] + S^{2-} \rightarrow ZnS:Cu$$

The concentration of the used MB solution was 5 ppm, while the concentration of ZnS:Cu nanoparticles were 30 $mgL^{-1}$for all experiments. The reaction MB solution was analyzed using UV–vis spectrophotometer. The degradation percentage (D%) of MB was calculated by the following equation [27]:

$$D\% = \frac{C_0 - C}{C_0} \times 100$$

where D, C_0 and C are the percent degradation, initial concentration of MB (with unit mgL^{-1}) and the concentration of MB after the treatments, respectively.

The effects of the presence of different on photocatalytic activity of MB were investigated under UV irradiation for different reaction times (2, 4 and 6 h), and results were compared, as shown in Figure 4. The photocatalytic efficiency of ZnS nanoparticles with different concentration of Cu ions compared to reaction times are listed in Table 1.

Table 1: Photocatalytic efficiency of ZnS nanoparticles with different concentrations of Cu regarding to reaction times.

Cu concentration (%)	D (%) reaction time = 2 h	D (%) reaction time = 4 h	D (%) reaction time = 6 h
0	0	0	0
0.5	43	56	65
1	51	69	77
2	65	73	85
5	40	55	59
10	28	41	50

As shown in Figure 4, $Zn_{0.98}Cu_{0.02}S$ nanoparticles exhibit the best photocatalytic decomposition efficiency in all reaction times. In 2 h of exposure time, the degradation of MB by this sample was 65%, and it reached 73% in 4 h. After 6 h of exposure to UV light, the decomposition efficiency of MB reached its maximum value of 85%. This improved degradation may be due to the specific surface area of these nanoparticles. On the other hand, the turtleback ZnS:Cu (2 wt%) nanoparticles have the most effective surface area.

In the doping process, the guest Cu atoms act as an acceptor in the ZnS lattice by creating an IB level. As a result, more free holes are generated which can contribute to the degradation process of MB.

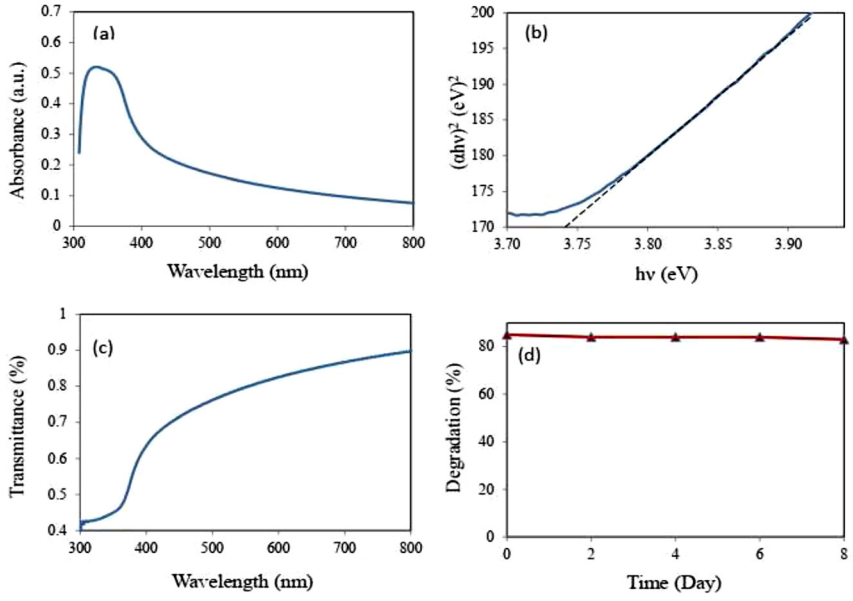

Figure 5: (a) The absorption, (b) The transmittance, (c) The plot (ahv) 2 versus hv to calculate the optical band gap energy (*Eg*) and (d) The cycle stability of nanoparticles with 2% of Cu concentration with reaction time of 6 h of ZnS:Cu (2%).

But a decrease in efficiency was observed when the higher concentrations of Cu ions were used. However, with further increase in Cu concentration (>2 wt%), nanoparticles show a great tendency to aggregate due to high surface energy combined with their high surface area-to-volume ratio [28].

Meanwhile, comparing the photocatalytic activity of ZnS:Cu nanoparticles and ZnS:Cu thin films [22], indicates that Cu-doped ZnS nanoparticles are better catalytic activity than thin films.

Figure 5(a) shows the optical absorption spectrum of ZnS:Cu(2%) in the range of 300–800 nm. Regarding Figure 5(a), it exhibits a peak in the short-wavelength region (about 350 nm). This absorption spectrum was used to evaluate the optical band gap energy (E_g) of nanoparticles. For this reason, the standard equation of $(\alpha h\nu)^2 = A(h\nu - E_g)$ for the direct band gap of semiconductor nanoparticles was used in Figure 5(b).

Figure 5(b) shows the transmittance of ZnS:Cu(2%) which exceeds 90% in the visible spectral region. The difference to 100% transmittance is mainly due to the losses by reflection. To evaluate the catalyst performance, the cycle stability of nanoparticles with 2% of Cu concentration with reaction time of 6 h was examined. According to Figure 5(d), the degradation will be reduced about 2% after eight working days. This reduction shows the cycle stability of nanoparticles which will be an important index to evaluate catalyst performance.

4 Conclusion

ZnS:Cu nanoparticles are better than thin films in degradation. The decomposition of MB was 85% in the presence of $Zn_{0.98}Cu_{0.02}S$ nanoparticles when exposed to UV–light for 6 h, while it was 56% in the presence of $Zn_{0.98}Cu_{0.02}S$ thin film when exposed to UV–light for the same period. Experimental results showed that the availability of surface to absorb more molecules of MB was achieved at 2 wt% Cu doping concentration.

The ZnS:Cu photocatalysis was proved to be an efficient material to remove the pollutants from industrial wastewaters and convert to non-toxic compounds.

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