

## Photo-catalytic Degradation of Methyl Orange In Water on CuS-Cu<sub>2</sub>S Powders

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**ABSTRACT:** Nano-CuS powders were synthesized with chemical solution method. XRD and SEM and spectrophotometry were used for characterization of the CuS powders. XRD analysis indicated that tetragonal CuS was the main phase with particle size of 16.2nm and little Cu<sub>2</sub>S phase was present. Scanning electron microscopy (SEM) analysis revealed that powder was plate like and had very little aspect ratio in morphology. The photo catalytic properties of CuS-Cu<sub>2</sub>S powders were studied. Methyl orange in water were rapidly decomposed with sunlight irradiation. Benzyl in preliminary production of methyl orange can also be photo-decomposed under sunlight irradiation and can fast be photo decomposed at higher pH condition.

**Key words:** Methyl orange, Degradation, Photo catalysis

### INTRODUCTION

Decontaminants of organic matter is important topic in environment engineering. Some method has been used on photo catalytic decomposition of the organic contaminants using photo catalyst, such as nano TiO<sub>2</sub>. Many organic contaminants contain benzyl that is of low effective to be decomposed using some photo catalysts. To improve photo catalytic property many works have been made including finding out new photo catalyst.

The CuS is a semiconductor with a short band gap closed to Si and large absorption coefficient in wide range of UV-infrared light. It has been used for photovoltaic cells in form of film and single crystal. However the CuS materials have not been reported as photo catalysts previously.

CuS powders have been syntheses with various processes, including corrosion-assisted reaction method (Tezuka, *et al.*, 2007 and Kalyanikutty, *et al.*, 2006) hydro-gel-assisted method (Puspitasari, *et al.*, 2006), chemical solution process (Liu, *et al.*, 2007; Roy and Srivastava, 2007 and Ji, *et al.*, 2005), hydrothermal reaction method (Ni, *et al.*, 2007 and Deng, *et*

*al.*, 2006). Shape and morphology of the particle can be controlled by using different method or different surfactant and organic template. In present paper we report chemical solution synthesis of CuS platelets and its photo catalytic features in destruction of methyl orange

### MATERIALS & METHODS

Method of preparing the CuS powders was similar to that mentioned in the literature<sup>[3,4]</sup>. Appropriate CuCl<sub>2</sub> was respectively dissolved in distilled water and HCl aqueous of pH<2, then (NH<sub>4</sub>)<sub>2</sub>S solution was slowly added in two CuCl<sub>2</sub> solutions with constant stirring, respectively. The black precipitations were fast formed. The precursor were then filtered and washed repeatedly with distilled water until pH=7. The precipitations were then dried at 100 °C for 4 h. The phase identification of the powders was conducted at room temperature using X-Ray diffractometer (XRD, CuK<sub>α1</sub>, λ=0.15406 nm, Model No. D/Max-2200PC, Rigaku, Japan). The phase and the particle size of powders were determined with the Jade5 analysis software that was provided with X-Ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-

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6700F, Japan) was used to analyze the particles morphology and the agglomeration of the powders.

In this study, methyl orange was used as a photo catalytic substrate to study photo degradation on the CuS powders. Photodecomposition experiments were performed in glass beaker. In each experiment, 100ml methyl orange solutions at concentration of  $6 \times 10^{-6}$  M were added to 50mg CuS in the breakers and dispersed with ultrasonic generator (UG, 40 kHz, Modal No: KQ-5200DE, China) at 50 W. To investigate the effect of pH value on photo catalysis on the CuS powders, two initial pH (pH=7 and pH=9) of the methyl orange solution were used in this experiment. The solution with pH=9 was achieved by adding NaOH aqueous solution to the initial solution with pH=7. Sunlight was used as irradiation light resources. The absorption spectra of methyl orange solutions before and after irradiation for different time were measured on UV-265FW spectrophotometer.

## RESULTS & DISCUSSION

The CuS powders prepared by chemical solution method were soft powders and deep black in color. The XRD patterns of CuS powders are shown in Figure1 which indicated that the powder were consist of tetragonal CuS and little  $\text{Cu}_2\text{S}$  and a particle size of the powders were 17.2nm for pH=3 and 19.1nm for pH=7 that were determined with strong peak (301) at  $2\theta=48.3^\circ$  of the CuS

phase. SEM micrograph of CuS powders is shown in Fig. 2 which indicated that particles exhibited much small tetragonal platelets with 1-3nm of thickness and 100-300 nm of width. The very small aspect ratio in morphology can provided large special surface area for the powders.

Photo degradation of methyl orange solutions on the CuS- $\text{Cu}_2\text{S}$  powder was studied in the experiments. In the absorption profile of methyl orange solution at a range of ultraviolet – visible light, there are two primary peaks, one is color peak at  $\sim 465$  nm, and another is characteristic peak of benzyl at  $\sim 192$  nm. The absorbance variations of methyl orange solution with irradiation time are shown in Fig. 3. It is clear that the methyl orange in water can be photo degraded on the CuS powder and rate of the degradation was increased with increasing the irradiation time. When pH=7 the adsorption peak of the methyl orange solution at  $\sim 465$  nm was faster than that at  $\sim 192$  nm. However when then pH was increased from 7 to 9, two adsorption peaks of methyl orange solution were decreased nearly at a same rate. This can be explained as follow. For many semiconductors, as the pH increases the positions of the bands shift upward with respect to vacuum, i.e., the potential of photo generated electrons becomes more negative or “more reducing”. Decomposition of benzyl is easier in reducing catalysis than in oxide catalysis.

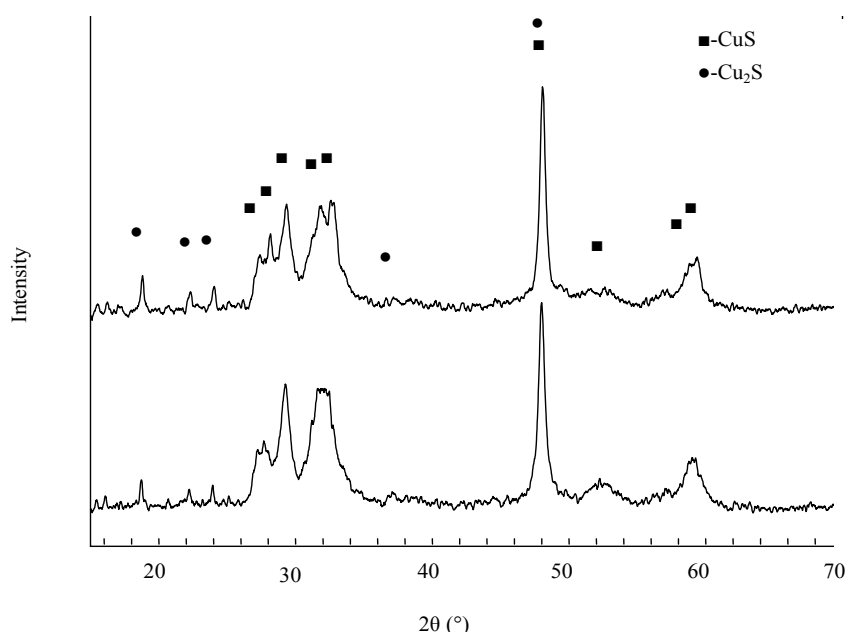


Fig. 1. XRD patterns of CuS- $\text{Cu}_2\text{S}$  powders

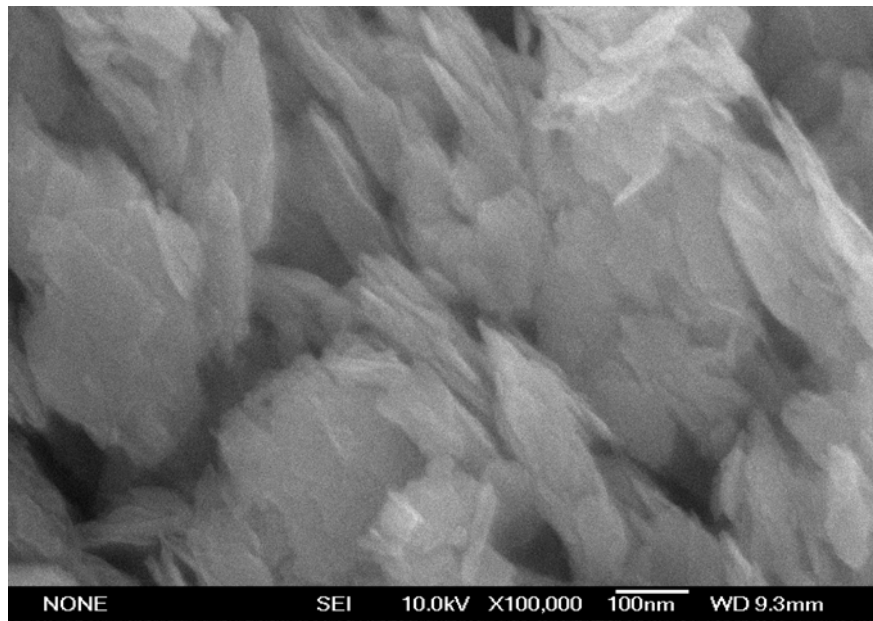


Fig. 2. SEM micrograph of CuS powders

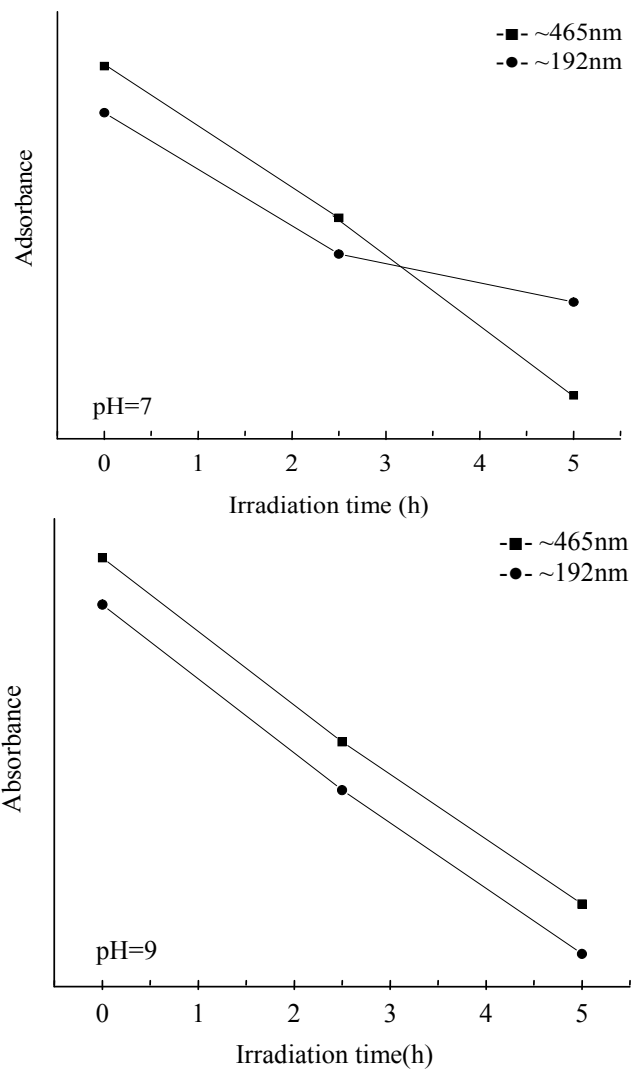


Fig. 3. Absorbance variations of methyl orange solution with irradiation time

Decomposition rate of methyl orange were larger and the benzyl in preliminary decomposed production of methyl orange and can be further decomposed at higher pH condition on the CuS semiconductor photo catalyst. In general, product of preliminary photodecomposition of many organic contaminants containing benzyl on many photo catalysts, concluding TiO<sub>2</sub> powders, is benzene and various substituted benzene that are also detrimental to human health and the environment. The fast decomposition of benzyl on the CuS powders in alkaline condition is of significance importance to decontaminant of aquatic environment.

### CONCLUSION

The tetragonal plate like CuS powders were efficiently synthesized with chemical methods. The powders have a very thin plate like morphology provided large surface area and a good photo degradation property. The correlations between photo catalytic activity and CuS powder and the pH value of the substrate solution were shown. Methyl orange can be photo degraded on the CuS powders. The benzyl in preliminary decomposed production of methyl orange can be fast photo degraded in alkaline condition. Strong and wide light adsorption of CuS make it very suitable for photo-catalyst application.

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