Photocatalytic Behaviour Of ZnS For Dye Degradation

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Abstract: Recently, transition metal sulphides, in particular ZnS have been intensively studied because of its unique Catalytic functions. These studies have revealed that ZnS nanocrystal are good photo catalysts due to rapid generation of electron –hole pair by photo-excitation. By adding surfactant in synthesis of ZnS, it has been observed that there is phase transition occurs from cubic to wurtzite. In the present work, ZnS is prepared by hydrothermal process using Ethylene diamine as surfactant. Prepared sample were characterized by X-ray diffractions (XRD), XPS, UV/VIS spectra were recorded for evaluation of photo physical properties. The photo activity of prepared ZnS with surfactant was accessed by photo catalytic decomposition of industrial waste under UV irradiation. Under the same condition photocatalytic activity of ZnS without surfactant was also examined. The ZnS with surfactant shows higher catalytic activity compare to ZnS without surfactant.

Keywords: ZnS, Congo Red, Methelyne blue , Bio-dye ,Photocatyalatic activity

INTRODUCTION

Photocatalytic activity of wide band gap semiconductor has been intensively studied as their applicability in various aspects such as their ability to simultaneously produce solar energy and drive chemical reactions via photoexcited charge carriers and electronic activated electronic states. Amongst various compound semiconductor, ZnS is extensively attended due to its robust performance, nontoxicity and chemical stability. ZnS is a promising material for different applications such as photocatalysts, photodetectors, gas sensors, piezoelectric sensors and ultraviolet lasers [1-3]. Morphology and size of the wide gap semiconductors like ZnS play very important role in the process like photo catalysis due to rapid electron-hole pair generation by photo-excitation. [4-5] These directly manipulate band gap of semiconductor with variation of surface to volume ratio, which ultimately enhance the redox potential. [6].

EXPERIMENTAL

Materials: Zinc actate Zn (AC)₂, Ethylene diamine (C₂H₄(NH₂)₂), thiourea (NH₂(SNH₂)), All the precursors were GR grade and procured from Merck (India) with 98% purity.

PREPARATION OF ZNS WITHOUT SURFACTANT

ZnS without surfactant were prepared by synthesis process, 50 ml of D.I. water added to 8.07796 g zinc acetate Zn (AC)₂ stirred upto 15 min. 3.0448 g thiourea added to mixture, again stirred for 10 minute. Then mixture was transferred to autoclave and heated at 200°c for 4 hrs. The mixture was cooled, filtered and washed several times with D.I water, then product was dried at room temperature to obtain ZnS.
SYNTHESIS OF ZnS WITH SURFACTANT

Synthesis route of ZnS with surfactant contains 25 ml of ethylenedia-amine added to 25 ml of DI water. Then stirred for 5 minute. After ward add 8.7796g ZnS to mixture and mixture again stirred for 15 minute. Add 3.0448g thiourea solution, stirred mixture for 10 minute. After this, solution transfer to autoclave and heated at 120ºc for 4 hrs. The mixture was cooled, filtered and washed several times with DI water. The sample was dried at room temperature to obtain powder of ZnS with surfactant which appear white in colour. The same process was followed for different percentage (20%, 40%, 50%, 90%) of ethylenediamine as surfactant.

RESULTS AND DISCUSSION

FIGURE 1: XRD of ZnS samples synthesized by using EN as surfactant and solvent having its 0%, 20%, 30%, 50%, and 90% in water

FIGURE 2: Increase of % Relative Intensity of XRD peak with EN

FIGURE 3: Rietveld refinement of XRD pattern of (a) ZnS cubic (b) ZnS Wurtzite

FIGURE 1 shows the XRD patterns of ZnS prepared by using ethylenediamine (EN) as a surfactant. For the sample without EN and 30% EN, the diffraction peaks are observed at 29.0°, 48.1°, and 57.0°. These peaks are identified due to (111), (220), and (311) planes cubic structures of ZnS (JCPDS No. 05-0566). For 30% EN, four new peaks are emerging out at 2θ = 27.37°, 30.75°, 40.06°, and 52.37° with three old peaks overlapping at 29.36°, 48.63°, and 57.27°. All the peaks are recognized with planes (100), (002), (101), (102), (110), (103), and (112) of the wurtzite phase of ZnS (JCPDS No. 36-1450).

Also wurtzite phase is detected for 50% EN and 90% EN. All the diffraction peaks of the sample are matched well with the wurtzite phase of ZnS crystal, indicating that the wurtzite phase has been formed in the sample with
the presence of EN. With increasing EN concentration, the relative intensity (I(hkl)/I(002)) of the new peaks due to (100), (101), (102), and (103) planes is found to be increasing shown in FIGURE 2.

For more structural clarification, all XRD data are refined by using Rietveld refinement full prof program. The fitting was performed by using the ZnS cubic structure with space group of F-43m and ZnS Wurtzite with a space group of P 6_3 mc. Rietveld fitted XRD of ZnS cubic and ZnS wurtzite are shown in FIGURE 3 (a, & b)

The SEM image of as-synthesized ZnS nanoparticles with and without surfactant are shown in FIGURE 4 a & b, respectively. The microstructural analysis shows that the ZnS grains for both the cases are almost spherical with homogeneous and uniform grain size distribution. The mean particles sizes are found below 100 nm. Particles size of ZnS-synthesized with EN is less than without EN. The usage of EN causes stabilization of the small particles and the inhibition of the agglomeration.

FIGURE 4: SEM Image of (a) Cubic ZnS and (b) Wurtzite ZnS

FIGURE 5: XPS of the as-synthesized ZnS-EN samples, (a) survey scan, (b) S 2p, (c) Zn 2p
The XPS data of the ZnS without and with a different percentage of EN, over a wide range of binding energy (0−1200 eV), are shown in FIGURE 5 (a).

It is evident that the elements Zn, S, C, O, and N (except in ZnS sample without EN) are present in the samples. The S 2p and Zn 2p detailed regions are shown in FIGURE 5 (b) and (c). There is no considerable variations in the binding energy values of the XPS peaks and hence not given here. Further, it is found that the ZnS ratio for the 0% EN sample is equal to 3.8, whereas for other samples it is equal to 2.0. Thus, all the samples are excess in Zn or sulfur deficient [71]
photocatalytic activity of ZnS for the degradation of MB and CR and Bio dyes, visible light assisted photocatalysis have been done in presence of natural light for this photocatalytic reaction. The concentration of dye is traced by monitoring the intensity measured at wavelength in nm of different dyes. We observed decrease the intensity of absorption peak with increasing the concentration of ZnS. This clearly shows decolouration of MB, CR and Bio dye in presence of ZnS cubic shown in FIGURE 6. and ZnS Wurtzite in FIGURE 7.

FIGURE 8 (a) and (b) shows photodegradation efficiency as a function of dopant content is obtained around 80% for CR and MB dyes by ZnS-cubic NPs, however for BD dye (Bio dye). it is found ZnS-cubic and Wurtzite, exhibits different rate of photodegradation for different dyes. The percentage of surfactant in ZnS are found affecting on photodegradation efficiency. It can be attributed to microstructural effect.

CONCLUSIONS

The photo degradation of industrial waste in presence of ZnS without and with surfactant are systematically monitored by UV-Vis spectrometer. In Summary, XRD confirmed the surfactant induced phase transition of ZnS. (ZnS cubic has transform to ZnS wurtzite by adding ethylene dia-amine as surfactant).

REFERENCES