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Structural and optical studies of undoped and copper doped zinc sulphide nanoparticles for photocatalytic application

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ABSTRACT

Photocatalytic activity of semiconductor nanoparticles for their potential application in the area of photocatalysis provides clean source for degradation of organic pollutants. With the aim to utilize it efficiently in photocatalytic degradation of organic pollutants, zinc sulphide nanoparticles capped with thioglycerol and doped with copper ($Zn_{1-x}Cu_xS$; $x = 0$, 0.01, 0.02, 0.03 and 0.04) were synthesized using simple chemical precipitation route. Structural studies were done using X-ray diffraction (XRD) technique. Morphological features of as prepared samples were recorded by high resolution transmission electron microscopy (HRTEM). Fourier transform infrared (FTIR) studies were done to confirm the presence of thioglycerol on the surface of doped ZnS. UV–Vis and photoluminescence studies were carried out to study the effect of doping on optical properties of synthesized material. Degradation of crystal violet has been carried out to investigate the effect of Cu doping on photocatalytic activity of ZnS. It is observed that Cu doping has enhanced the photocatalytic activity of ZnS. Further, UV irradiation study of thioglycerol capped ZnS NPs has been carried out to investigate its effect on photocatalytic performance of the material. The obtained results are interesting and may find applications in photocatalytic degradation of organic pollutants on large scale and also in other related areas.

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1. Introduction

In recent years, the synthesis of binary metal chalcogenide nanoparticles (NPs), such as cadmium and zinc chalcogenides (CdSe, CdTe and ZnS) has become a rapidly growing area in materials chemistry to develop fundamental understanding for their practical applications such as light-emitting devices, lasers, photocatalysts and as biological fluorescence labels [1–5]. Despite the numerous applications of cadmium based nanostructures (NSs), these NSs can cause the release of cadmium under certain conditions [6,7]. It causes harmful effects, particularly in view of environmental regulations, so the applicability of Cd-containing NSs is restricted. However, ZnS is the suitable alternative to this problem as it contains light metal Zn. Due to their non-toxic nature; ZnS nanocrystals are ideally suited for applications in biological labeling and diagnostics [8]. Further, among the II–V1 semiconductors, ZnS is a well-known luminescent material having a wide and direct band gap of 3.54 eV (cubic zinc blende phase). For their application in photocatalysis, it possesses high negative reduction potential of excited electrons due to its higher conduction band position in aqueous solution as compared to other extensively studied photocatalysts [9]. Also, this material shows good photocatalytic activity due to trapped holes arising from surface defects on the sulphides [10]. Till now, considerable efforts have been made to control the size and morphology of ZnS NSs so that these could be efficiently utilized in related applications [11–13]. As a result, it has emerged as a promising candidate for its diverse applications in fabrication of optical and optoelectrical devices [3,4]. Owing to its large band gap, ZnS can easily host different transition metal ions acting as luminescent centres [14]. In undoped ZnS, band gap can be modified by intercalating dopant energy levels in the host. Further, doping of ZnS with transition metal ions such as Cu ions offers a way to trap charge carriers and extends the lifetime of one or both of the charge carriers. Consequently, dopants are expected to enhance the efficiency of the photocatalyst [15]. Till now, various attempts have been made to make ZnS as an efficient photocatalyst in near visible or visible region [15–18]. Jang et al. [16] synthesized N-doped ZnS based nanohybrid at 150 °C. The N-doped ZnS had the decreased band gap compared to pure ZnS and it exhibited good photocatalytic activity in the degradation of Orange II dye under visible light irradiation. Muruganandham et al. [17] synthesized N, C codoped ZnS photocatalyst. It showed a significant AO7 degradation under visible light irradiation, demonstrating that the synthesized material is effective visible light-responsive photocatalysts. In his work, Mohamed investigated the photocatalytic activity of thin films of ZnS:Cu^{2+} NPs towards methylene blue dye [15]. Enhanced photocatalytic activity of Cu doped ZnS films was attributed to the reason that Cu^{2+} ion can be reduced to a Cu^{+} ion by a hole produced with semiconductor (SC) which is strongly oxidative. Pourtedal et al. [18] studied the effect of Mn, Ni, Cu:ZnS NPs in photocatalytic degradation of methylene blue and safranin. In their work, emphasis was made on the photocatalytic application of materials. The photocatalytic activity obtained was in the order

$$\text{ZnS} < \text{ZnS macrocrystalline} < \text{ZnS nanocrystalline} < \text{ZnMnS} < \text{ZnNiS} < \text{ZnCuS}$$

The synthesis conditions, characteristics and concentrations of dopants are responsible for particular properties and efficiencies of SC NPs. So, it becomes necessary to understand the role of dopant on structural, optical and photocatalytic properties of doped SC NPs from the view point of physics as well as its applications in related areas. Although, material preparation and characterization of Cu doped ZnS NPs have been carried out on large scale [19–21], but, the investigation related to the effect of dopant concentration on optical and photocatalytic properties of these NPs is very limited [22,23] and still need more understanding. Also, to the best of our knowledge, the model organic pollutant selected in this work (crystal violet) has not been degraded yet by employing doped ZnS NPs as a photocatalyst. Thus in the present work, the emphasis was to synthesize Cu doped ZnS NPs with different dopant concentrations and to study its effect on structural, optical and photocatalytic properties of ZnS NPs. Further, an attempt is made to study the effect of UV irradiation on photocatalyst properties.

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