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Efficient photocatalytic degradation of rhodamine-B by Fe doped CuS diluted magnetic semiconductor nanoparticles under the simulated sunlight irradiation

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ABSTRACT

The present work is planned for a simple, inexpensive and efficient approach for the synthesis of $Cu_{1-x}Fe_xS$ (x = 0.00, 0.01, 0.03, 0.05 and 0.07) nanoparticles via simplistic chemical co-precipitation route by using ethylene diamine tetra acetic acid (EDTA) as a capping molecules. As synthesized nanoparticles were used as competent catalysts for degradation of rhodamine-B organic dye pollutant. The properties of prepared samples were analyzed with energy dispersive analysis of X-rays (EDAX), X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible optical absorption spectroscopy, Fourier transform infrared (FTIR) spectra, Raman spectra and vibrating sample magnetometer (VSM). EDAX spectra corroborated the existence of Fe in prepared nanoparticles within close proximity to stoichiometric ratio. XRD, FTIR and Raman patterns affirmed that configuration of single phase hexagonal crystal structure as that of ($P6_3/mmc$) CuS, without impurity crystals. The average particle size estimated by TEM scrutiny is in the assortment of 5–10 nm. UV-visible optical absorption measurements showed that band gap narrowing with increasing the Fe doping concentration. VSM measurements revealed that 3% Fe doped CuS nanoparticles exhibited strong ferromagnetism at room temperature and changeover of magnetic signs from ferromagnetic to the paramagnetic nature with increasing the Fe doping concentration in CuS host lattice. Among all Fe doped CuS nanoparticles, 3% Fe inclusion CuS sample shows better photocatalytic performance in decomposition of RhB compared with the pristine CuS. Thus as synthesized $Cu_{0.97}Fe_{0.03}S$ nanocatalysts are tremendously realistic compounds for photocatalytic fictionalization in the direction of organic dye degradation under visible light.

1. Introduction

Environmental pollution has become one of the demanding challenges to the sustainable improvement of modern human society, owing to industrialization, population growth and urbanization. Currently, pollution in natural water is considerable health risk and continues to threaten both eco-system and quality of human life. Particularly, majority of the pharmaceutical, fabric, paper, flesh, paints and photochemical industries utilize the numerous artificial dyes for various functionalities, which are poisonous, non-recyclable and are contrasting to straight degradation through sunlight. Consequently they can be visible as persistent contaminants. The release and succeeding assembly of these poisonous complexes in water media create awful hazard to the surroundings. Number of research groups and scientists have made several attempts to eradicate these dangerous pigments from wastewater and pursued numerous techniques like centrifugation, coagulation, sedimentation, filtration, adsorption and distillation. However these techniques consist of many side effects. Concurrently, photocatalysis with semiconductor has been extensively deliberated as

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a feasible water splitting process. Despite the fact that the TiO_2/UV process has been most frequently studied for this purpose. Even though TiO_2 has diverse advantages such as superhydrophilicity, strong oxidation ability, chemical stability and it's nontoxic, inexpensive but the realistic job of TiO_2 is limited due its little photon consumption efficiency and need of excitation source under the ultraviolet region, which accounts for only a minute portion of sunlight [1–5]. Hence, visible light active photocatalysts are being dynamically sought for better consumption of solar light.

However, at present among the plethora of various visible active photocatalysts like CuS [6], WO_3 [7], $BiVO_4$ [7], CdS [8], AgI/RGO [9], Ag_3PO_4 [10] and Ag_3PO_4/WO_3 [11], covellite phase copper monosulfide (CuS), is one of the non stoichiometric and stoichiometric p-type semiconductor, low cost and earth-abundant material. It has been identified as a vital compound for resourceful class of applications in energy storage, gas sensors, solid state solar-cells, optoelectronic devices, biosensors, lithium ion batteries and photocatalysis [12–17]. Especially for the visible light photocatalytic application Cu_xS is a very suitable material due to its wide range of optimum band gap (1.2–2.4 eV) with the stoichiometric composition (x = 1.0–2.0). The main cause behind this attention can be endorsed to the high surface area to volume ratio, as well as adequate exterior active locations of CuS material. Hence these surface active sites consent to improved reactions between the reactive pollutants and the surface of CuS supporting for better photocatalytic performance. Furthermore, due to suitable band gap and being evidence for strong ferromagnetism at room temperature through inclusion with transition metal ions (Fe, Co, Ni, Cr and Mn) with CuS is one of the important pathways to provide the considered necessary structure to create dilute magnetic semiconductors intended for spintronic device application [18,19].

Up to now, several approaches have been made to enhance the efficiency of CuS material for photocatalytic organic dyes degradation and succeeding clean environment. In this direction J. Yu et al. [17] reported ion-exchange method which provides new insight into the fabrication of composite hollow spheres, while Yingwei Zhang et al. [20] investigated one-pot synthesis of CuS/reduced graphene oxide nanocomposites with enhanced photocatalytic performance. J. Kundu [21] et al. reported controlled synthesis and catalytic activity of copper sulfide nanostructured assemblies with different morphologies and M. Basu et al. [22] observed degradation of different dyes through indoor lighting by CuS hexagonal stacked plates. G. Nie et al. [23] reported synthesis of polyacrylonitrile modified CuS composite towards the reusability application in catalysis of organic dye decomposition. Y. Wang et al. [24] observed photocatalytic properties of graphene modified CuS nanocrystals. Qu wei Shu et al. [25] reported decomposition of organic dye pollutant in the absence of light through CuS caved super structures. Nevertheless, the photocatalytic performance is partial through recombination between the photo generated charge carriers. In general for swift degradation of the organic dyes, the utilization of electron hole pairs are play important role, on the other hand the photocatalytic activity is suppressed due to recombination of electron hole pair. For this reason, in order to enhance the photocatalytic activity, diverse new approaches have been attempted such as modifying the structure, increase the external surface area, creating enhanced morphological properties, or generating structure defects. Besides, the most triumphant path to enhance the photocatalytic activity is by doping the CuS semiconductor with the transition metals, such as Fe, Co and Ni. Because, when doping the magnetic transition metal ion to the host lattice, they generates new defect locations which work as an electron pond and restrains the photo generated hole-electrons pair recombination. In consequence, created electrons and holes are shifted towards catalyst surface where they contribute in reduction reaction with the organic pigment (RhB) reactive species as well as help in the enhancement of photocatalytic activity.

Further, in the direction of investigation for visible light active magnetic photocatalyst semiconductors, passionate research movement has been devoted due to their excellent performance under the solar light. Senapati et al. found improved photocatalytic activity with simple magnetic separation of a $CoFe_2O_4$–ZnS composite [26], while Lianli Zou et al. reported fabrication and dye removal performance of magnetic $CuFe_2O_4$@CeO_2 nanofibers with specific surface area of 64.12 m^2/g and M_s of 20.51 A m^2/kg [27]. Anshu et al. reported the appropriateness of cobalt doped ZnS nanoparticles for recyclable photocatalysts [28].

In previous work, our research group also found the effect of magnetic properties on the photocatalytic performance of synthesized samples and achieved better photocatalytic activity in 5% Co doped CuS nanoparticles for which magnetization is also good [29]. Predominantly, 5% Co doped CuS nanoparticles exhibited a significant degree of photo-catalytic degradation ability; it took only 60 min for the complete degradation of RhB organic pollutant. To the best of our knowledge, there are no testimonies on Fe doped CuS nanoparticles in the view of academic and applied attention. In order to depict new panorama in this field, to afford the magnetic photocatalysts for accomplishing the organic impurities decomposition along with a simple exclusion and convalescence from slurry systems and to provide a soaring surface area intended for better reaction, we herein report on pure and 1%, 3%, 5% and 7% Fe doped CuS nanoparticles, which were synthesized through chemical precipitation method. The effect of Fe inclusion on the morphological, structural, optical, magnetic and photocatalytic properties of CuS host lattice is reported. In addition to the tremendous photocatalytic degradation possessions, the prepared nanoparticles also showed strong room temperature ferromagnetism with Fe doping, which implies that Fe doped CuS diluted magnetic semiconductor samples may also find application in fabrication of spintronic devices.

2. Experimental

2.1. Preparation of pure and Fe doped CuS nanoparticles

In the present work analytical grade chemicals were used devoid of additional purification and deionised water was employed as a reaction media in all preparation stages. For the present synthesized nanoparticles, $Cu(CO_2CH_3)_2 \cdot 2H_2O$, $FeCl_2 \cdot 4H_2O$ and Na_2S chemicals were used as resource constituents for Cu, Fe and S respectively. $Cu_{1-x}Fe_xS$ (x = 0.00, 0.01, 0.03, 0.05 and 0.07) nanoparticles be prepared with easy wet chemical co-precipitation technique and similar to our earlier work [31]. In a few words, as per the stoichiometric ratio all the source materials were dissolved in aqueous media with concentration of 0.2 M and made stirring more than 25 min. Further, the anionic solution of sodium sulphide precursors was taken in burette and appended drop wise to the solution of copper and Fe cationic source solutions. In order to reduce agglomeration and control the size of prepared nanostructures 0.5 mL of capping agent (EDTA) be mixed to the ending solution as well as stirred over 8 h. By using de ionized water and methanol, ensuing precipitate was cleaned through number of times. Finally the resultant compound was dehydrated at 110 °C over 8 h and consequently synthesized in to good quality of nanoparticles.

2.2. Characterization

The synthesized pure and 1%, 3%, 5% and 7% Fe doped CuS nanoparticles were analyzed by different characterization studies.