Journal of Environmental Chemical Engineering 4 (2016) 808–817

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Synthesis of CdS nanoparticles using different sulfide ion precursors: Formation mechanism and photocatalytic degradation of Acid Blue-29

Nida Qutub, Bilal Masood Pirzada, Khalid Umar, Suhail Sabir*

Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form 21 October 2015
Accepted 24 October 2015
Available online 29 October 2015

Keywords:
CdS
Different sulphide ion source
Chemical precipitation
Structure–electronic properties
Photocatalysis
Acid Blue-29

ABSTRACT

Cadmium sulphide (CdS) nanoparticles were synthesized by different combinations of chemical precursors using H_2S, Na_2S and $(NH_4)_2S$ as sulphide ion sources. The reactions were carried out by a single pot chemical precipitation method under ambient conditions. The X-ray diffraction (XRD) patterns obtained for the synthesized nanoparticles (NPs) were used to determine their crystal structure and the crystallite size. The average particle sizes of the synthesized nanoparticles were determined by transmission electron microscopy, UV–vis spectra and XRD techniques. Electron dispersive spectroscopy and Fourier transform infrared spectroscopy were used to investigate the purity of the synthesized CdS nanoparticles. The smaller particle size for CdS was obtained with Na_2S, followed by H_2S and $(NH_4)_2S$ and that the quantization in the band gap was directly in correlation with decreased particle size effects. In addition, mixed phase of wurtzite–zinc blende was synthesized with H_2S, while phase pure zinc blende and wurtzite phase was obtained with Na_2S and $(NH_4)_2S$, respectively. The series of synthesized CdS nanoparticles were exploited for photocatalytic degradation of an organic dye derivative, Acid Blue-29, under visible light and the effect of different precursor combinations on photocatalytic efficiency was analysed. An increase in photocatalytic rate was observed by the decrease in particle size on using different sulfide ion precursors, which can be attributed to the increase in the catalyst surface area, band gap and powerful redox capability. The effect of different sulphide ion sources on the structural and photocatalytic properties was compared and optimized by the above studies.

1. Introduction

Since last two decades photocatalytic degradation using semiconductors (such as TiO_2, CdS, Fe_2O_3, ZnS, WO_3, Bi_2WO_6 and ZnO) have been done for effective photocatalytic degradation of organic pollutants in water [a,b,c,d].

CdS is one of the most technologically important class of semiconductor materials, due to its bulk bandgap of 2.42 eV that leads to a whole range of colors in the visible region when the size is reduced. CdS nanoparticles has been extensively utilized for photocatalytic water splitting and hydrogen production [a,b,c] and for photodegradation of organic or inorganic pollutants in water and air [4] under visible light. The conduction band edge of these materials is sufficiently more negative than the reduction potential of protons and the band gap is relatively narrow, thus they can efficiently absorb visible light [5,6]. However, the reported quantum efficiency of CdS photocatalytic reactions is fairly poor due to the fast recombination of photo-generated charge carriers. Various attempts have been made to improve the efficiency of the photocatalytic activity of CdS, like changing the surface structure of CdS nanoparticles by controlling morphology (size and structure) [7], the deposition of CdS to Nafion membranes or polymers to get homogeneously distributed quantum sized CdS nanoparticles [8,9,10] or the doping of transition metal ions into CdS, and the coupling of two semiconductors [11–13]. Recently, CNTs (carbon nano tubes) decorated with CdS nanoparticles and nanowires have been reported [8,14–16] as photocalatysts.

CdS is an II–VI semiconductor (band gap energy 2.42 eV) exhibiting intrinsic n-type of conductivity caused by sulfur vacancies due to the cadmium surplus [a,b]. CdS has three types of crystal structures; wurtzite, zinc blende and high pressure rock-salt phase. The nanoparticles (NPs) of CdS show unique altered physical, chemical and structural properties from the bulk. Due to wide range of applications in different fields of life, CdS NPs have been synthesized extensively. Depending upon the reaction conditions, same material can crystallize in different structures on size reduction [18]. Thus, CdS is particularly an attractive system for practicing synthetic chemistry for nanocrystals and for

* Corresponding author.
E-mail address: drsuhailsabir@gmail.com (S. Sabir).

http://dx.doi.org/10.1016/j.jece.2015.10.031
2213-3437/

understanding the chemistry, growth history of nanomaterials and also in various technical applications [15,19].

Among various synthesis techniques, chemical precipitation method [20] is the most extensively used method for fabrication of CdS NPs due to its ease, simplicity and small reaction time. CdS NPs can easily aggregate in aqueous solution during preparation process resulting in rather lower efficiency. Hence, efforts are done to enhance the stability of CdS NPs in aqueous media. The size and stability of the synthesized NPs are controlled either by restricting the reaction space within matrices such as zeolites, glasses, silica, polymers, reverse micelles and vesicles [21], or by using stabilizers and capping agents, like thiols, phosphates, phosphine oxides, mercaptoacetic acid, thiourea, and thioglycerol [15,22] or the reaction precursors like sulphide ion sources. Solvents are known to affect the kinetics and equilibria of reactions, the spectroscopic properties of solutes and even the facets present on crystals [23].

In the present work, CdS NPs were synthesized by different combinations of chemical precursors using H_2S, Na_2S and $(NH_4)_2S$ as source of S^{2-} ions. CdS NPs were grown by simple chemical precipitation reactions in aqueous medium at room temperature. The effect of stabilizers on the stability and size of CdS NPs was studied. The effect of different S^{2-} ion sources ($(NH_4)_2S$, H_2S and Na_2S) on the size of nanoparticles, respective band gaps and crystalline structure were studied. Finally, the series of synthesized nanoparticles were exploited for the degradation of Acid Blue 29 (AB-29), under visible light. The photocatalytic efficiency of the synthesized NPs, using different reactant combinations, were compared and optimized.

2. Materials and methods

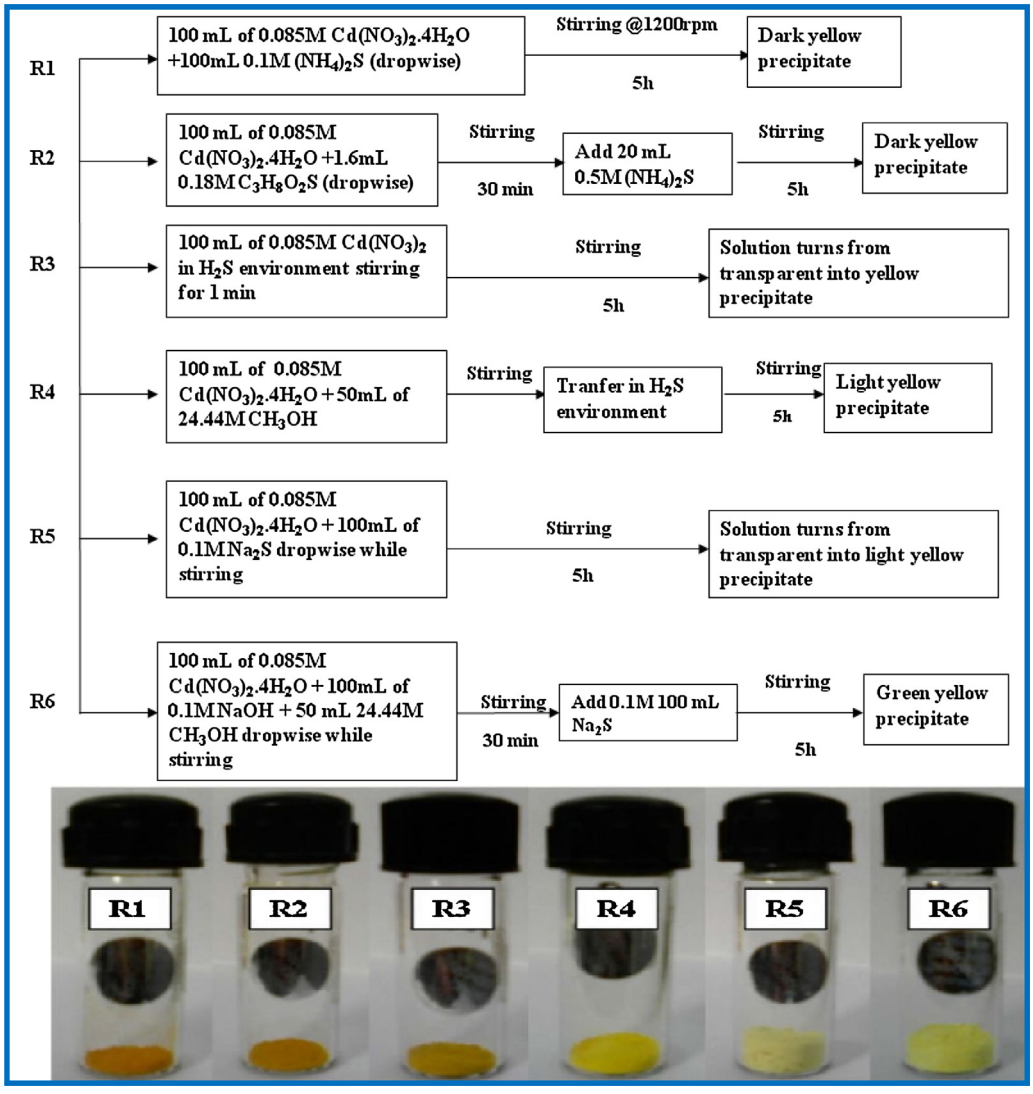
2.1. Materials

Cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$), ammonium sulphide ($(NH_4)_2Sx$), 1-thioglycerol ($C_3H_8O_2S$), methanol, sodium sulphide (Na_2S), sodium hydroxide (NaOH) were all obtained from Fischer Scientific, India. Hydrogen sulphide (H_2S) was prepared by a known procedure using Kipp's apparatus with ferrous sulphate ($FeSO_4$) turnings and sulphuric acid (H_2SO_4).

Acid Blue 29 ($C_{22}H_{14}N_6Na_2O_9S_2$, mol. wt. 616,49 g/mol) was obtained from Sigma–Aldrich, India (CAS-No.: 5850-35-1). It is an azo dye with 40% dye content and was found useful in laboratory chemicals and manufacture of substances like in textile industry and staining.

Different stabilizing agents were used with different precursors as each precursor has a different reaction mode and rate.

All chemicals were of analytical grade and were used without any further purification.



Scheme 1. Flow chart showing the course of reactions R1, R2, R3, R4, R5 and R6.