

Effect of transition metal ion doping on the photocatalytic activity of ZnS quantum dots: Synthesis, characterization, and application for dye decolorization

Hamid Reza Rajabi*, Mohammad Farsi

Chemistry Department, Yasouj University, Yasouj 75918-74831, Iran

ARTICLE INFO

Article history:

Received 25 October 2014

Received in revised form 27 January 2015

Accepted 28 January 2015

Available online 29 January 2015

Keywords:

Dopant effect

Quantum dots

Methyl violet

Salt effect

Nanophotocatalyst

ABSTRACT

In this research, green and aqueous based synthesis routes were performed for chemical preparation of pure and transition metal ions doped ZnS quantum dots at room temperature. Doping of ZnS QDs by three transition metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} ions) as dopants have been investigated by various techniques. In the optical absorption studies, a broad absorption band in the wavelength range of 280–300 nm clearly reveals quantum size effect in ZnS QDs. The crystal structure and the approximate size of QDs were measured by XRD pattern. The average particle size of QDs was found to be around 1–3 nm. In addition, the photocatalytic activities of the prepared ZnS QDs as their abilities to remove methyl violet (MV) cationic dye, as a model molecule, were studied. Effect of the experimental parameters, such as the type of dopant and the amount of QDs, pH of the initial dye solution, irradiation time, ionic strength of reaction media, and initial dye concentration on the decolorization efficiency (DE) of QDs as green nano-semiconductors were studied. The results demonstrated that doped QDs (for 5% of dopants) effectively bleached out MV, showing positive photocatalytic enhancement over pure ZnS nanoparticles.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the application of nanophotocatalyst in the removal of contaminants in air and wastewater has attracted the researchers' interest [1]. Photocatalytic processes that decompose organic contaminants into simple inorganic species have attracted attention to their various environmental applications [2]. Recently, photocatalytic decolorization of pollutants using quantum dots (QDs), as efficient and novel nanophotocatalysts for decolorization of organic pollutants, have received considerable attention. They have garnered widespread interest among a multitude of research groups as they exhibit higher extinction coefficients, higher quantum yields, less photobleaching, broad absorption, and narrow emissions, which can be tuned with size [3].

Moreover, QDs get more and more attention because their confinement by the excited electrons and holes leads to optical and electronic properties different from those in bulk semiconductors [4]. On the other hand, surface modification QDs can change their optical, chemical, and photocatalytic properties. Being coated on any surface and capability of the band gap to be tuned by changing

the size, and the shape of the particle are the potential advantages of colloidal QDs [5]. It can also cause an improvement in the photostability of QDs, the generation of new traps on the surface of the QD leading to the appearance and efficiency of light induced reactions occurring on the surface of QDs. For the above reason, QDs have great potential in analytical applications in aqueous [4].

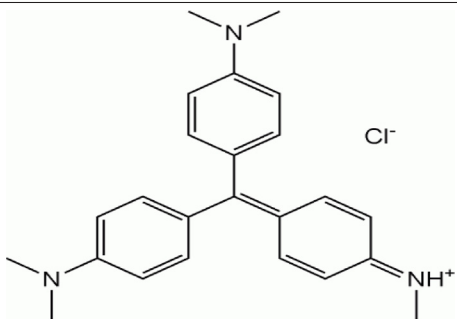
Among semiconductor QDs, zinc sulfide (ZnS) QD has been extensively researched. ZnS exhibits a wide range of novel structures by controlling the growth rate along different directions. ZnS quantum dots have been synthesized by many researchers with the aid of capping agents, the result of which exhibited strong confinement effects [6]. ZnS is chemically more stable, nontoxic and more environmentally safe than other II–VI compound semiconductors [7]. Hence, it has more potential applications in biological detection and treatment of wastewaters. In particular, due to a wide direct and large band gap, and a large exciton binding energy of ZnS, it is a good host for doping [8].

Doping with proper element is widely used as an effective method to tune surface states, energy levels, and electrical, optical, structural and magnetic properties of semiconducting materials [9–11]. The critical role that dopants play in semiconductor devices has stimulated research on the properties and the potential applications of semiconductor nanocrystals, or colloidal quantum dots, doped with intentional impurities [12]. The use of intentional

* Corresponding author. Tel.: +98 741 2242164; fax: +98 741 2242164.

E-mail address: h.rajabi@mail.yu.ac.ir (H.R. Rajabi).

Table 1
Characteristics of dye.

Dye	Methyl violet (MV)
Structure	
$\lambda_{\max}$	585 nm
Molecular formula	$C_{24}H_{28}N_3Cl$
Molar mass	393.95 g mol ⁻¹
CAS number	8004-87-3
C.I. number	42535

impurities, or dopants, to control the behavior of materials lies at the heart of many technologies. For this reason, researchers have begun to explore how dopants can influence semiconductor nanocrystals, crystallites a few nanometers in scale with unusual and size-specific optical and electronic behavior [13]. The energy from absorbed photons can be efficiently transferred to the impurity, quickly localizing the excitation and suppressing undesirable reactions on the nanocrystal surface [14]. Incorporation of ZnS with other transition metals such as manganese, nickel, and copper can have a beneficial effect on the photoreactivity of photocatalysts [15]. These doped ZnS semiconductor materials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, and optical sensors [16]. We have reported earlier that iron [17] and manganese [18] ions can be successfully doped in ZnS nanoparticles even at room temperature by a simple and efficient chemical precipitation method.

The aim of this research was to study the effect of transition metal ion doping on the photocatalytic activity of ZnS QDs, as green and efficient nanophotocatalysts. The researchers have adopted a wet chemical route of semiconductor nanoparticle synthesis. The techniques employed to characterize the materials were UV-vis spectroscopy, XRD and TEM. After characterization, the prepared QDs' efficiency in removing a cationic dye (i.e., methyl violet) from aqueous solution was investigated.

2. Experimental

2.1. Materials and apparatus

All chemical reagents were analytical grade, prepared from Merck and/or Fluka Companies. $Na_2S \cdot 5H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 5H_2O$, and 2-hydroxyethanthiol (2-mercaptoethanol; $HOCH_2CH_2SH$), all purchased from Merck company, were of the highest purity available. The methyl violet dye ($C_{24}H_{28}N_3Cl$) was a laboratory reagent grade, purchased from Sigma-Aldrich Company (Table 1). The pH of sample solution was adjusted by aqueous hydrochloric acid and sodium hydroxide solutions. All solutions were prepared in double distilled water.

All pH-metric measurements were made on a digital pH-meter Metrohm Model-827 fitted with a glass electrode, which was previously standardized with buffers of known pH in acidic and alkaline medium. Optical absorption spectra were obtained using PerkinElmer UV-vis double beam LAMBDA-25 spectrophotometer. Transmission electron microscopic images of the prepared

pure and iron doped QDs were recorded using a Zeiss-EM10C-100 KV. The X-ray diffraction (XRD) pattern was obtained using STOE-Stady-mp Diffractometer with Cu K α source ($\lambda = 1.541786 \text{ \AA}$). In photocatalyst process, irradiation was carried out with a 36 W mercury lamp (Philips) with the emitted light at 254 nm.

2.2. Synthesis of quantum dots

The researchers have adopted a chemical route of semiconductor nanoparticles synthesis in which 2-hydroxyethanthiol capping agent is added to the reacting solutions during the synthesis. Capping agents are used to arrest the growth of nanoparticles and to stabilize them against aggregation [19]. They also modify the structural, morphological, and optical properties of nanoparticles [6]. Synthesis of pure ZnS nanoparticles, doped with Mn^{2+} , Ni^{2+} , and Co^{2+} dopants has been carried out using a wet chemical precipitation method [20]. The advantages of using this method are: simplicity, low-cost, availability of the equipments, and capability of yielding nanoparticles of highest purity [21]. Procedure in brief is as follows. Firstly, 100 mL of 0.1 mol L^{-1} aqueous solution of zinc nitrate containing 0.05 mole fractions of Mn^{2+} , Ni^{2+} , and Co^{2+} dopants (0.0, and 0.05 in $Zn_{1-x}M_xS$; where M is metal ion) added to a three necked flask. After it, 100 ml of 2-hydroxyethanthiol aqueous solution as capping agent (0.1 mol L^{-1}) was added drop-wise to the above solution, under magnetic stirring and nitrogen atmosphere. Next, 100 ml of $Na_2S \cdot 5H_2O$, 0.1 mol L^{-1} solution was added to the flask, under vigorous stirring. The resulting viz., zinc sulphide nanoparticles that were capped with 2-hydroxyethanthiol chains began to precipitate when solution stirring was stopped. The precipitate was washed several times in water to remove unreacted materials. Finally, by centrifuging and drying the washed precipitate, free standing powders of nanoparticles were obtained (Scheme 1). The powders are highly stable and do not show any coalescence or agglomeration even after several months.

According to the previous studies, size and the growth mechanism of the nanocrystals are highly dependent on the nature and concentration of capping agent [17,22]. It is generally accepted that the capping agent coordinates with the cations. The bonding should neither be too strong nor too weak to allow for dynamic coupling in which the coordinating molecules attach to and de-attach from the growing nanocrystals. In this way the particle can grow to its final size which is determined by the type and the concentration of the capping agent. If the binding between the cations and the capping agent becomes stronger, the particles can reach smaller final sizes [23]. As the concentration is lower, the incomplete capping of the surface by capping molecules allows for a faster particle growth [22]. Here, in the preparation step of QDs, the concentration of capping agent was kept constant.

2.3. Quantum dots based photodecolorization process of MV dye

The photocatalytic experiments were conducted using $Zn_{1-x}M_xS$ (M: Mn^{2+} , Ni^{2+} , Co^{2+} ions) QDs, to photocatalytically degrade MV in water solution. For photocatalytic decolorization, a stock aqueous solution (100 ppm) of MV was prepared. Aqueous dye solutions with different concentrations were prepared from the above stock solutions and the pH of all solutions was adjusted at desired values. Then, the final reaction solutions were prepared by adding nanophotocatalysts into each of a 100 ml of MV solution. The solutions were irradiated with UV lamp to provide energy to excite QDs loading. The distance between the solution and UV source was constant, 10 cm, in all experiments. At certain time intervals, the samples were taken and the remaining dyes were analyzed, using spectrophotometric technique. Before and after UV irradiation, suitable aliquots of the sample were withdrawn and analyzed after centrifugation. The decrease of absorbance value

Download English Version:

<https://daneshyari.com/en/article/65182>

Download Persian Version:

<https://daneshyari.com/article/65182>

[Daneshyari.com](https://daneshyari.com)