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Study of capping agent effect on the structural, optical and photocatalytic properties of zinc sulfide quantum dots

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In this work, the effect of capping agent type on the structural, optical and photocatalytic properties of pure zinc sulfide (ZnS) quantum dots (QDs) has been investigated. ZnS QDs were prepared by a simple, fast and water based chemical precipitation method, in the presence of various capping agents including 2-mercaptoethanol, thiourea, and L-cysteine. The obtained QDs have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), and UV–visible absorption spectroscopy. The results revealed that the optical absorption band of ZnS nanostructures varied by capping agents. In the photocatalytic investigations, the prepared ZnS QDs were applied for the photodecolorization of crystal violet (CV) as a model molecule. Influence of affecting parameters on the decolorization efficiency of the capped ZnS QDs was studied and optimized. The results indicated that the prepared QDs can effectively remove different concentrations of CV dye at alkaline pH, in the presence of low concentrations of QDs. According to the photocatalytic results, the presented method can be considered as a green, quick and efficient strategy for photobleaching of organic pollutants based on the high performance photocatalytic behavior of ZnS QDs capped by different capping agents.

1. Introduction

In the recent years, Quantum dots (QDs) as nano-scale luminescent inorganic semiconductor nanocrystals with physical dimensions smaller than the exciton Bohr radius [1], have had a significant impact on research in many fields across the physical, chemical, and biological sciences [2]. Due to the unique electro-optical properties of QDs such as size-tunable light emission, simultaneous excitation of multiple fluorescence colors, high signal brightness, long-term photostability, and multiplex capabilities, they has been pained many attention by the researchers [3,4].

Other advances key of QDs, recent advances on the surface chemistry of QDs by conjugation with appropriate functional molecules [5]. The surface modification of QDs can enhance their luminescent quantum yields, their stability and prevent them from aggregating [6]. Moreover, by surface modifications of QDs, it is possible to make QDs available for interactions with target analytes [7], for various applications. However, modification of QDs by highly toxic organic reagents may restrict the application of this method [8]. Therefore, proper surface modification is a critical challenge to keep QDs colloidal and photostable under intracellular or intercellular conditions.

Up to now, various surface modifications of QDs have been explored by different capping or functionalized agents such as thioglycolic acid [9], thioacetamide [10], L-cysteine [11,12], 3-mercaptopropionic acid [13], trioctylphosphine [14], trioctylphosphine oxide [15], mercaptosilane [16], glutathione [17], dihydrolipoic acid [18],bovine serum albumin [19], and polymer coating [20]. Functionalization of the QDs surface by a chemical agent can alter morphology, particle size, toxicity, mechanical stability, optical properties and as well as their photocatalytic activities.

On the other hands, removal of industrial dyes as one of the largest sources of water contamination due to their toxic and carcinogenic metabolites has long been a major environmental problem all over the world [21,22]. Many efforts for removal of organic pollutant dyes from wastewaters have been carried out by such as carbon adsorption, filtration, chemical precipitation, photodegradation, coagulation, ozone oxidation biodegradation, electrolytic chemical treatment, and membrane technology [23]. However, decolorization from dye-contaminated wastewaters by these methods is usually non-destructive, inefficient, costly and result in the production of secondary waste products [24]. Therefore, it is necessary to investigate innovative methods for treatment of dye containing wastewaters [25]. In recent years, quantum dot assisted photodecolorization process has been demonstrated as an efficient and green method for removal of resistant organic pollutants from water [26,27]. Among of nanomaterials, Zinc-based QDs may be environmentally friendly except at

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very high concentrations when it may become toxic to humans [28]. Due to the absence of the toxic elements in zinc sulfide (ZnS) QD, therefore, ZnS has been considered as the most popular choice for application in biomedical and photocatalytic applications, as well as due to its high surface area as compared to their bulk counterparts [26–29].

The aim of this work was to study the effect of different capping agents including 2-mercaptoethanol, thiourea, and L-cysteine on the structural, optical and photocatalytic properties of ZnS quantum dots as nanophotocatalyst. A water based chemical precipitation route was applied to the synthesis of nano-sized ZnS particles, at room temperature. After comparative characterization by different techniques, photocatalytic activities of QDs modified with different capping agents were investigated as nanophotocatalysts, based on their efficiency for decolorization of crystal violet as a model molecule.

2. Experimental

2.1. Materials and apparatus

In the synthesis of ZnS QDs, zinc nitrate ($Zn(NO_3)_2 \cdot 4H_2O$) and different capping agents including 2-hydroxyethanthiol, thiourea, and L-cysteine (all from Merck) were of the highest purity available and used without any further purification. Characteristic of the used capping agents are presented in Table 1. Crystal violet dye (Table 2) and sodium sulfide ($Na_2S \cdot 9H_2O$; 98%; w/w) were of laboratory reagent grade and purchased from Sigma-Aldrich Company. Aqueous solutions of hydrochloric acid and sodium hydroxide were used for pH adjustment of the solutions.

All UV–vis absorbance spectra were recorded with a UV–vis spectrometer (Perkin-Elmer UV–vis spectrophotometer LAMBDA-25). Transmission electron microscopic images were obtained with a Zeiss-EM10C-100 kV. X-ray diffraction (XRD) patterns were obtained using German Bruker D8Advanced Diffractometer with Cu Kα source ($\lambda = 1.5406$ Å). pH of sample solutions was controlled with a Metrohm 692 pH-meter. A mercury lamp (36 W/m^2, Philips) was used as UV light irradiation source in photocatalytic studies.

2.2. Water based synthesis of ZnS QDs capped by different agents

Synthesis of ZnS QDs was carried out in the presence of different capping agents at room temperature, without applying of any organic solvent, as follows [30,31]: firstly, an aqueous solution of zinc nitrate as a Zn^{2+} ion source (250 mL, 0.1 mol L^{-1}) was inserted in a three necked flask. Then, an aqueous solution of capping agent (i.e. 2-mercaptoethanol, thiourea, and L-cysteine) with the same concentration and volume was placed into a dropping funnel. Aqueous solution of capping agent was added to the Zn^{2+} aqueous solution drop by drop with magnetic stirring and nitrogen atmosphere purging. After finishing the capping agent solution, precipitating agent (i.e. sulfide ions) was added drop-wise to the flask, under vigorous stirring. The precipitated ZnS nanoparticles were then centrifuged, washed and dried at 50° C.

Table 1
Characteristics of the used capping agents.

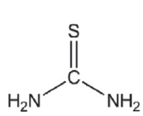
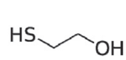
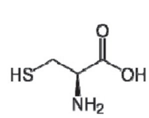
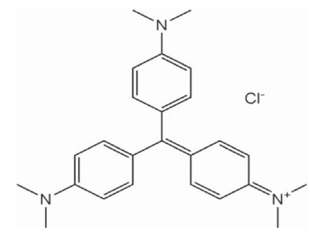
Name	Thiourea	2-mercaptoethanol	l-cysteine
Chemical structure			
Molecular formula	CH_4N_2S	C_2H_6OS	$C_3H_7NO_2S$

Table 2
Characteristic of the dye.

Name of the selected dye	Crystal Violet (CV)
Chemical structure	
λ_{max} (at alkaline pH)	590 nm
Molecular formula	$C_{25}H_{30}N_3Cl$
Molar mass	407.979 g mol^{-1}
CAS number	548-62-9

2.3. Comparative study of photocatalytic ability of different ZnS QDs

In the photodegradation step, 250 mL aqueous solution of CV dye with certain concentration was prepared, and the optimum amount of QDs was added. After adjustment the pH by hydrochloric acid and sodium hydroxide solutions, the suspension was sonicated for 15 min before illumination for dispersing the QDs in the solution. The aqueous suspension was then put under constant stirring in dark for 1 h to achieve the adsorption equilibrium. In all experiments, the distance between the solution surface and UV light source was constant 15 cm, to avoid the heating effect. The stable suspension was then exposed to the UV-radiation with continuous magnetic stirring, then, the UV lamp was switched on to initiate the reaction. At regular time intervals, about 2 ml of suspension solution was sampled, centrifuged, and the remaining dye was analyzed, by using spectrophotometric technique. The concentration of the dye in the reaction mixture at the different reaction time was monitored by spectrophotometry by measuring the absorption intensity at $\lambda_{max} = 590$ nm with a calibration curve, decolorization efficiency (DE%), as well as the activity of the nanophotocatalysts was calculated [26].

3. Results and discussion

3.1. Structural properties of QDs

Fig. 1(A)–(C) exhibits TEM images of ZnS QDs capped by different capping agents, prepared by the chemical precipitation method. As seen, due to small particle size of ZnS QDs, it is difficult to exactly determine the size of the particles; however, as revealed by TEM images, the obtained particles have a mean diameter of below 5 nm. It is possible to suggest that the capping agents covering the ZnS particles, and therefore, the particles don't coalesce to form bigger particles, even after an extensive period of time [32]. However,