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Enhancement of visible light photocatalytic activity of ZnS and CdS nanoparticles based on organic and inorganic coating

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ABSTRACT

Coating of ZnS and CdS nanoparticles with organic and inorganic materials can extend their light absorption in the visible region and their stability against photo-corrosion. Such materials could emerge as excellent photocatalysts for the elimination of pollutants from aqueous media using solar energy. In this study, PVP (polyvinyl pyrrolidone)-capped ZnS and CdS nanoparticles, ZnS/CdS and CdS/ZnS core shell nanoparticles were synthesized by microwave irradiation method and characterized using different techniques. The XRD patterns exhibited cubic and hexagonal structures for coated ZnS and CdS nanoparticles, respectively. Morphological evaluation of TEM images showed that the nanoparticles are generally spherical in shape. The UV–visible spectra confirmed a shift in the band gap of coated nanoparticles to longer or shorter wavelengths due to size and potential-well effects. The photocatalytic activity of nanoparticles toward dye degradation under visible light was found to be improved after coating. PVP-capped ZnS and CdS exhibited an enhancement in the initial methylene blue degradation efficiency by a factor of about 1.3. ZnS nanoparticles coated by CdS displayed the initial efficiency 3.2 times higher than bare ZnS. The maximum dye removal was obtained in presence of CdS/ZnS core shells which is 1.4 times more efficient than bare CdS.

1. Introduction

Efficient photocatalytic processes have been proven to be of a great contribution in treatment of environmental deprivation. Photocatalytic oxidation of organic and biological molecules is one of the most efficient methods for alleviating the negative environmental impact of hazardous wastes and toxic pollutants in aqueous media [1–5]. The superiority of photocatalytic technique in wastewater treatment is due to its advantages over the traditional techniques such as quick oxidation, high efficiency, no formation of polycyclic products and oxidation of pollutants in the low levels [6]. Photocatalysis is a process based on electron–hole pairs created in semiconductor materials by the absorption of photons with energy more than or equal to its band gap, causing excitation of valence band electrons into the conduction band and creates the electron–hole pairs. Such electron–hole pairs can further generate free radicals in the system to redox the compounds absorbed on the surface of a photocatalyst. The resulting free-radicals such as hydroxyl (·OH) is a very efficient oxidizer of organic materials and can degrade pollutants in the medium [7–12].

Accordingly, the photocatalytic activity of semiconductor materials can be controlled by three key factors: (1) light absorption property, (2) rate of reduction and oxidation of reaction substrates by, respectively, electron and hole, and (3) rate of electron–hole recombination. These factors are mostly governed by the crystal structure, particle size and surface texture of the semiconductor. The structure of semiconductors depends upon the synthesis methods and conditions. The size effects originate primarily from the size quantization in nanoscale that can change the band gap of semiconductor and size-related surface characteristics such as surface area and defects. The redox potential of the reaction substrates, which adsorbed on the surface varies to the surface chemical structure and the amount of adsorbed substrates, depends more directly on the specific surface area. Thereby the high surface area to volume ratio of nanosized particles appears to be an important parameter for seeking to design and engineer photocatalytic materials in nanoscale [5,13].

An ideal photocatalytic material would operate on a combination of high activity regarding the relevant process of interest and high efficiency of solar energy conversion. The use of solar irradiation to energize photocatalyst materials is environmentally appealing for its self-sufficient energy and permits the design of a water treatment which is simple, robust and inexpensive to set up and run. The photocatayst materials should also be stable over a

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long period of the operation. However, no such material or system currently ever exists to satisfy all these requirements [5,14].

Semiconductor nanostructures such as ZnS and CdS nanoparticles bear the potential to have many of these right entities. ZnS nanocrystals are believed to be one of effective photocatalysts, resulting from its rapid generation of electron–hole pairs and the highly negative redox potentials of excited electrons; however its photocatalytic performance under visible light, the most part of the solar energy, was restricted due to its wide band gap and intrinsic defects [15–19]. CdS, on the other hand, can easily absorb the evoking light in the visible region; however, it is prone to photocorrosion in the long-term photocatalytic reactions [20,21]. Since these nanoparticles exhibit properties that can be controlled by changing size, doping, surface modification or sensitization, their reactivity can be altered or enhanced. Their redox potential and density of active surface states for chemical reactions and photon absorption depend on their particle size. Moreover, doping a certain amount of metal ions as well as deposition of organic or inorganic materials on the surface of semiconductor nanoparticles can enhance their photocatalytic activity by interfacial charge transfer and electronic interaction between the surface attachment and the host semiconductor. The photocorrosion can also be minimized by dispersing the nanosize crystallites over the surface of a polymeric support or by coupling of two semiconductors in a core–shell formation [22,23].

In the present work, we have attempted to provide improvement in visible light photocatalytic activity of microwave synthesized ZnS and CdS nanoparticles via coating their surface by organic or inorganic materials. Microwave irradiation method is a facile and effective synthetic strategy to produce high purity perfect nanocrystals under mild conditions at reasonable cost and environmentally friendly. The organic passivation of nanoparticles was performed using a water dispersible polymer, polyvinyl pyrrolidone (PVP), in a one pot reaction. For the inorganic passivation of ZnS and CdS nanoparticles, a layer of given thickness of CdS and ZnS, respectively, have been deposited on the surface of nanoparticles using a two steps synthesis procedure. The obtained nanocomposites were characterized with several routine techniques and their photocatalytic performance was studied and compared by employing the photodegradation of methylene blue (MB) under visible light irradiation in terms of degradation efficiency and kinetic rate constant of photocatalysis.

2. Experimental section

2.1. Materials

The starting materials for the synthesis of II–VI sulfur semiconductor nanoparticles were zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$; R&M Chemical), cadmium chloride ($CdCl_2{\cdot}9H_2O$; Acros Organics) and thioacetamide (CH_3CSNH_2; Sigma-Aldrich) as zinc, cadmium and sulfur sources, respectively, polyvinyl pyrrolidone (PVP; Sigma-Aldrich) as capping agent and ethylene glycol ($C_2H_6O_2$; ALFA Chemical Co.), ethanol (C_2H_5OH; HmbG chemicals) and distilled water as solvents.

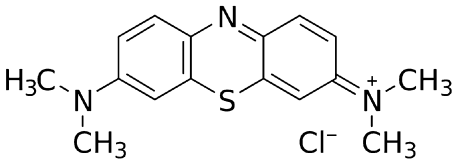
For photocatalytic reactions, methylene blue ($C_{16}H_{18}N_3SCl$; Sigma-Aldrich) was chosen as a pollutant in this study, due to its importance as dye in textile industries and in a variety of other applications and also its various harmful effects on human [4]. Its structure and characteristics are given in Table 1.

All the reagents and chemicals were of analytical grade products and used without further purification.

2.2. Preparation of PVP capped ZnS and CdS nanoparticles

In a typical procedure, 1 g of PVP was dissolved in 10 ml distilled water. Subsequently, 5 mM zinc acetate or cadmium chloride was added to the PVP solution under stirring (500 rpm) for 30 min. Next, 10 ml of aqueous sulfur source solution was added and stirred until a well-dissolved solution was obtained. The final solutions were put in a high power microwave oven (1100 W) operated using a pulse regime of 20% power for 30 min. The precipitates were centrifuged (3500 rpm, 5 min) and washed several times with distilled water and ethanol and dried in air at 60 °C for 24 h in a controlled environment.

Table 1
Structure and characteristics of methylene blue.

Dye	Methylene blue (MB)
Structure	
Molecular formula	$C_{16}H_{18}N_3SCl{\cdot}3H_2O$
λ_{max}	664 nm
M_w (g mol^{-1})	319.85
CAS number	7220-79-3

2.3. Preparation of ZnS/CdS and CdS/ZnS core shell nanoparticles

The core shell nanoparticles were fabricated in a two-step route: initial synthesis of core nanoparticles, followed by a purification step, and the subsequent shell growth reaction. In the first step the desired core material, ZnS or CdS nanoparticles, was synthesized by reaction of zinc and cadmium sources with sulfur source in ethylene glycol using microwave oven for 25 min with power of 20% by a pulse regime. The precipitates were centrifuged (3500 rpm, 5 min) and washed several times with distilled water and ethanol before drying in air at 60 °C for 24 h under control environment. In the next step of shell growth reaction, the shell precursors were dissolved in 40 ml ethanol and subsequently 5 mM of core nanoparticles was added to the ethanol solution and dispersed using sonication for 60 min at 40 °C. Then the solution was put in microwave oven for 25 min with power of 20%. During this step, a small number of monolayers of the shell material are deposited on the cores. The precipitates were centrifuged (3500 rpm, 5 min) and washed several times with distilled water and ethanol and dried in air at 60 °C for 24 h under control environment.

2.4. Characterizations

The products were characterized by X-ray powder diffraction (XRD) at a scanning rate of 5°/min in the 2θ range 10°–80° using a Philips X-ray diffractometer (N.V. Philips Analytical X-ray, Almelo) with Cu $K\alpha$ radiation ($\lambda = 0.1542$ nm). Energy dispersive X-ray (EDX) measurements were performed under a variable pressure scanning electron microscope (VPSEM, LEO 1455) with an Oxford INCA EDX 300 microanalysis attachment. The morphology and particle size were determined with a Hitachi H-7100 Transmission Electron Microscope (TEM) operating at an accelerating voltage of 100 kV. The optical properties of the nanocomposites were characterized using UV–vis spectroscopy on a Shimadzu UV–1650PC spectrophotometer.

2.5. Photocatalytic reaction

The photocatalytic degradation was performed by taking 0.6 L of 10 mg/L of MB solution in 1.0 L cylindrical Pyrex reactor containing 100 mg/L of catalyst. The solution was exposed to a 500-W halogen lamp as the visible light source (emission range of 400–800 nm