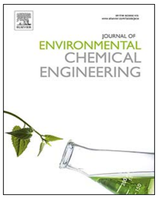
Journal of Environmental Chemical Engineering 6 (2018) 74–94

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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



SDS capped and PVA capped ZnO nanostructures with high photocatalytic performance toward photodegradation of reactive red (RR141) azo dye

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ARTICLE INFO

Keywords:
ZnO
Surfactant
SDS capped
Photocatalytic
Azo dyes

ABSTRACT

Two types of ZnO nanostructures have been synthesized successfully in high yield by using either sodium dodecylsulfate (SDS) or polyvinyl alcohol (PVA) as a capping agent *via* a facile and low temperture chemical precipitation method. The synthesized ZnO samples show well crystallized wurtzite hexagonal phase. The SDS surfactant played a crucial effect on morphology, specific surface area and photocatalytic performance of the ZnO photocatalyst. SDS capped ZnO with high specific surface area of 14.8 $m^2 g^{-1}$ shows much higher photocatalytic performance in comparision to that of PVA capped ZnO. Nearly 95% and 88% of reactive red (RR141) azo dye decomposed after irradiation for 240 min under UV light and 80 min under solar light, respectively. The photodegradation reaction follows the pseudo first-order kinetics with the high rate constant (k) of 0.04 min^{-1}. The SDS capped ZnO photocatalyst retains its original efficiency of about 87% even after the third cycles of reuse indicating the advantages of stability and reusability. Hole and hydroxyl radical are the two major reactive species involving in photodegradation of azo dye. ZnO nanostructures with SDS as a capping agent will be suitable for photodegradation of organic pollutants in the environmental protection. The method and ideas presented herein will potentially provide cheaper and cleaner means for treatment of a large volume of organic dyes. The photodegradation process can be performed very easily even under solar light irradiation. This offers some insight into the progress of technological applications related to the degradation of industrial dyes.

1. Introduction

A large variety of toxic residual organic dyes has been found in toxic wastewater effluents from different industries including textile, cosmetic, paper, leather, and phamacuetical industries. From the environmental point of view, some synthtic dyes are of serious concern due to their toxic and carcinogenic properties. Dye industry plays a major role in polluting the fresh water eco-system. About 15% of dyes were discharged into the environment during synthesis and processing. It was reported that azo dyes are the largest group (about 60–70%) of widely used synthetic dyes. Among the different class of dyes that are used, reactive dye wastewater has limited biodegradability in an aerobic environment. Reactive dyes are usually characterized by the presence of azo chromophores (−N═N−) or phthalocyanine chromophore (containing copper, nickel or other metals) and aromatic rings. These groups are considered toxic and mutagenic to living organism. In addition, both organic dyes and textile chemicals pose a dreadful threat for the ground water sources. Very small amounts of dyes in water (lower than 1 ppm for some dyes) are visible and undesirable [1–4]. Therefore, it has always been a matter of great concern to search for a cost-effective treatment of wastewater containing dissolved dyes and other organic chemicals. It has been reported that several techniques such as bio-electro-Fenton [5], sonoFenton [6], electro-Fenton processes [7–9], electrochemical oxidation [10], sonocatalysis [11], *etc.* have been used to treat the wastewater. In addition, the conventional method in particular adsoption method has been adopted to eradicate the dyes from wastewater [12–15]. These methods not only transfer the chemicals to solid state but also, in some cases, produce large slurries which in turn cause secondary pollution. All some drawbacks need to be overcome, *i.e.* an alternative method is needed.

Semiconductor nanostructured materials are of great important in both fundamental and potential applications in daily life. Interestingly, their properties are uniques and differ from those of the bulk counterparts. Semiconductor photocatalysis technology has been widly used to degrade pollutants and decompose water for producing hydrogen, due to the advantages of low energy-input, easy operation, clean and efficient. Photocatalytic oxidation has been used for photodegradation of organic pollutants and has become the focus of scientific research in

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https://doi.org/10.1016/j.jece.2017.11.066
Received 8 August 2017; Received in revised form 28 October 2017; Accepted 24 November 2017

environmental protection. This method provides the advantages of low operating costs, the possibility of eliminating complex compounds, no need for additional materials, using free solar energy and the ability to perform the process in ambient temperature and pressure. Many oxides and sulfides semiconducting nanomaterials have been prepared and applied to the above photocatalytic application. Zinc oxide (ZnO), one of the important II–VI semiconductors with large direct band gap of 3.37 eV, has been attracted wide attention due to its unique band structure and large exciton binding energy of about 60 meV with high potential to degrade the organic pollutants [16]. ZnO, a key smart material, is one of the most promising photocatalyst showing desirable properties such as high activity, ease in preparation, low toxicity, high thermal stability, excellent chemical and mechanical stability, environmental sustainability and low cost of production. Obviously, structure of photocatalyst is the main factor affecting its photocatlytic perfomance. In addition, it has been demonstrated that photocatalytic activity of ZnO nanostructures can be optimized by morphology control [17,18]. The structure, size, size distribution, and morphology of ZnO strongly depend on preparation method and experimental conditions. These parameters influence the properties of the synthsized nanomaterials. The above statements encourage us to develop convenient synthetic strategies for the synthesis of hierarchical ZnO structures. Up to now, many types of ZnO nanostructures such as nanorod arrays, nanofibers, thin films, flower-like microsctructures, and mesoporous nanoclusters have been prepared by various techniques such as ionic liquid assisted synthesis, plant extracted assisted green synthesis, atomic layer deposition (ALD), chemical bath deposition (CBD), electrochemical process, light-assisted growth, electrospinning, sol-gel, solvothermal, and hydrothermal method [19–28]. Moreover, in some cases the capping agents including organic polymers such as polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP) [18] are used as fuel in nanocrystal formation of ZnO. These materials also act as dispersing medium, and prevent agglomeration of particles. Surfactants have been used as capping agent as well [29,30]. The growth of the different morphological structures of ZnO largely depends on the relative stability of the growth and direction of crystal faces. In general, the presence of capping agent can change the growth rate in different crystal planes due to stabilization of a particular crystal facet by adsorption. The externally added surfactants or capping agents were adsorbed preferentially on some crystal planes of the growing particles. This ultimately changes the growth kinetics and relative stability of the crystal faces and hence either promotes or inhibits crystal growth in some particular crystal planes, resulting in the formation of anisotropic ZnO nanostructures. Photocatalytic performance of ZnO photocatalyst toward photodegradation of varous organic dyes including rhodamine 6 G [31], rose Bengal [32], Congo red [33], methyl orange [34], azure B [35], and methyl violet dye [36] has been reported. The photocatalytic reaction under UV light [37,38], visible light [39,40], and natural solar light irradiation [41–43] has been studied. In some cases, interestingly, photocatlysts based on binary [44–46] or ternary components [47–50] have been used.

Most of the synthesis techniques require high temperature, vacuum, or complicated controlling processes. Therefore, it is of great importance and necessity to develop a technique operating at mild reaction conditions. Chemical precipitation method has been proven to be versatile approach for preparation of various photocatalysts including ZnO due to the convenience and simplicity in the operation [30,38,40,51].

In this paper, we report the low temperature synthesis of ZnO nanostuctures *via* chemical precipitation method using either SDS surfactant or PVA as a capping agent. The process can be applied for a large-scale preparation of other II–VI group semiconductors. In addition, thermal and optical properties of the capped ZnO semiconductors have been investigated. PVA capped ZnO shows spherical morphology while SDS capped ZnO exhibits mainly thin plate-like nanostructures together with partially nanorod morphology. The photocatalytic activity study of these ZnO photocatalysts toward photodegradation of reactive red (RR141) azo dye, under UV light, visible light and solar light irradiation, showed that SDS capped ZnO exhibits superior photocatalytic performance in comparison to that of PVA capped ZnO sample. This is due to the thin plate-like and nanorod morphological structures with large specific surface area. In addition, the enhancement in photocatalytic activity found in this sample is also attributed to the improvement of charge separation at the interface. This results in not only lowering electron-hole recombination efficiency but also increasing the lifetime of the photogenerated exciton pairs. The ZnO semiconductor could be used as a very stable photocatalytic degradation material for removing of reactive red azo dye. The photodegradation efficiency of the photocatalyst was relatively unaffected for three cycles of use. This demonstrates its high stability and promising photocatalytic performance. Hole and hydroxyl radical are the two major reactive species involving in photodegradation of azo dye. Electron also made huge contribution toward photodegradation process but less than the contribution from both hole and hydroxyl radical. The idea for removing reactive red (RR141) azo dye from environmental wastewater by solar-light-driven photocatalytic process is very promising. Environmental problems can be solved very easily by utilization of solar energy.

2. Experimental sections

2.1. Materials

All analytical (AR) grade chemicals were used in this work without further purification. The de-ionized water was used throughout the experiment.

The reactive azo dye, C.I. Reactive Red 141 (RR141), obtained from DyStar Thai. Co. Ltd., was used. The structure of the dye is shown in Fig. 1. This dye shows the wavelength of maximum absorbance (λ_{max}) at 544 nm. The molecular weight and the solubility of the dye were found to be 1774 gmol^{-1} and 50 gL^{-1}, respectively.

2.2. Syntheses of ZnO nanostructures

2.2.1. SDS capped ZnO

In a typical synthesis, 0.1 M zinc nitrate hexahydrate [Zn

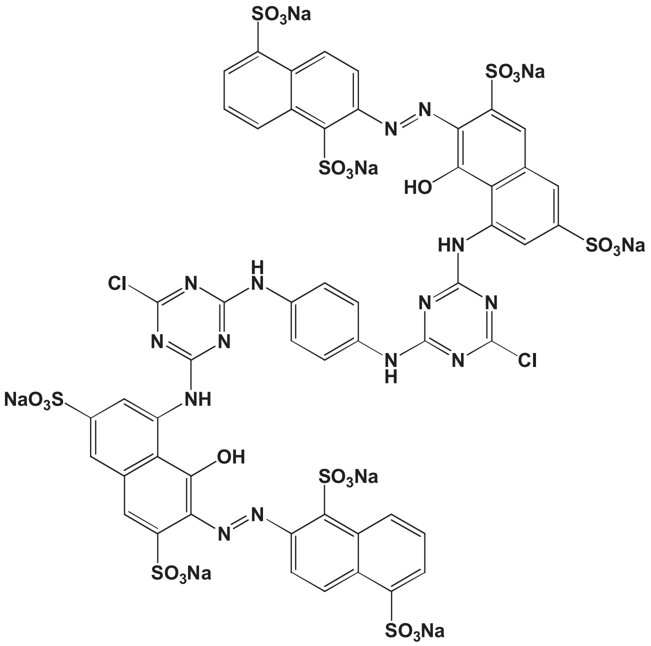

Fig. 1. Chemical structure of diazo C.I. Reactive Red (RR 141).