

Preparation of Metal Catalysts on Granule Glass for Degradation of Textile Dyes as Environmental Contaminants

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Abstract: Photocatalytic decolorization of azo-dyes in water has been examined in an external UV light irradiation using nanostructured of binary zincite catalyst on granule glass as a semiconductor photocatalyst. Nanostructure films of binary zincite have been prepared on granule glass by our technique. Their photocatalytic performances were tested for degradation of Azo dyes in solution under UV irradiation. The structure, surface and morphology properties of the nanostructured zincite film on granule glass have been investigated by XRD, SEM techniques. The results showed that the binary zincite film coated on glass surface have a very high photocatalytic performance under UV light.

Key words: Nano · azo dye · nanostructures · sol-gel chemistry · catalytic properties

INTRODUCTION

Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable. These effluents cause a lot of damage to the environment. Various chemical and physical processes such as precipitation, adsorption, air stripping, flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents. Water pollution is a major concern in many countries. Several methods of water purification have been practiced since many decades. Semiconductor photocatalysis is a promising technique, for photodegradation of various hazardous chemicals that are encountered in waste waters. The great significance of this technique is that, it can degrade (detoxify) various complex organic chemicals, which has not been addressed by several other methods of purification. The general classes of compounds that have been degraded by semiconductor photocatalysis include: alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, haloaromatics, polymers, surfactants, herbicides, pesticides and dyes. Heterogeneous photocatalytic oxidation (PCO) is a method to remove low concentrations of organic contaminants [1-5]. The UV light excites electrons from the valence to conduction band of the semiconductor catalyst leaving holes behind. The electrons-hole pairs can initiate redox reactions with surface species. The subject of semiconductor mediated

photocatalysis has gained much attention in recent years [6]. The degradation of toxic pollutants like phenols, surfactants and certain dyes has been observed to be efficiently catalysed by irradiated semiconductors. In a waste treatment application it would be simpler if the catalyst were immobilized, so the material would not have to be separated from solution. Sol-gel chemistry has recently evolved into a general and powerful approach for preparing inorganic materials. Thin films are one of the most important materials due to technological applications [7]. These wide variety of applications are including photoluminescence and transparent semiconductor [9], photocatalyst, piezoelectricity [10] gas sensors [11] UV light emitting devices [12, 13], varistors [14], Optical devices [15]. Thin films have been prepared by various techniques, such as physical vapor deposition [16], Chemical Vapor Deposition (CVD) [17] spray pyrolysis, sputtering [18, 19] Pulsed Laser Deposition (PLD) [20] and sol-gel method [21-27]. One of the most important advantages of sol-gel processing including, conventional thin film deposition techniques, are the ease of chemical composition control, low temperature annealing and homogeneous of sol solution, these advantages make sol-gel processing a very attractive method especially for preparation of thin films. Thin film photocatalysts with their high photocatalytic ability, high stability, convenient reuse, have received more and more attention. However, there has been little success in finding thin film

photocatalyst that can operate effectively as yet. As part of our goal produce binary zincite thin film on granule glass by sol-gel coating method and photoreaction of Direct Blue 256, Direct Red 81, Direct Yellow 86 and Direct Orange 39 on zincite thin film. In this paper, a commercial granule glass was successfully used as substrate to prepare nano-sized zincite thin film. The binary zincite/Glass films have been employed in photocatalytic decolorization of Direct Blue 256, Direct Red 81, Direct Yellow 86 and Direct Orange 39 azo dyes, in aqueous solutions. The result shows that the film is a new visible-driven photocatalyst with higher activity. It is very interesting and significant to research promising photocatalysts for high efficient utilization of solar energy for removal of hazardous material from water.

EXPERIMENTAL

Preparation of sol: All the chemicals were analytic grade reagents without further purification and purchased for Merk company. All dyes (C. I. Direct Blue 256, C. I. Direct Red 81, C. I. Direct Yellow 86 and C. I. Direct Orange 39) were obtained from Youhao (China). The coating substrate (granule glass) was pre-heated at 275°C for 10 min in air after each coating. The sol-gel coating was made usually a day after the sol solution was prepared.

Film deposition: Zincite thin film was supported on glass beads (diameter 3mm) by our method as follows. Glass beads were etched with dilute hydrofluoric acid (5% v/v) for 24 h and washed thoroughly with distilled water, making a rough surface for better contact of zincite thin film on the glass surface. Zincite binary sol was added to the glass beads placed in a funnel and the excess of binary zincite sol was removed. They were subsequently placed in the furnace, pre-heated at 275°C for 10 min and post-heated at 450°C for 1 hour. The deposition was repeated for 5 times to obtain films with different thickness.

Characterization techniques for thin films: The structure and crystalline size were determined by XRD diffraction (Bruker D8 advanced X-ray diffractometer: Cu K α radiation, Scan rate 0.03 2 θ s⁻¹). X-ray diffraction shows zincite structure with c-axis orientation (002). The surface of the films was observed by scanning electron microscopy (SEM) with a Philips XL30. Decolorization of dyes are measured by spectrophotometer (CECIL-CE7500).

Photoreactor and photocatalytic measurement: The photocatalytic decolorization experiments were carried out in a simple oxidation reactor, placed in a 25°C water bath. Granule glass with 5-layer that placed in 25 mL 25 ppm Dyes solution was irradiated with two 8W lamp (Philips; $\lambda=365\text{nm}$) placed 5 cm above the solutions. Concentration is measured by spectrophotometer (CECIL-CE7500). In all experiments 25 mL of 25 ppm dyes solution were used with stirring during the irradiation.

RESULTS AND DISCUSSION

Stability of sol: Increasing the water content and dilution of sol system and decrease the time of reflux may make the sol to gel immediately. The adding of MEA and water is to keep the sol solutions stable and clear for a long period and we found the sol that prepared with this composition it to be stable for many days.

Structure and morphology of nanostructure binary zincite on granule glass: The morphology and texture of nanostructure binary zincite on granule glass were affected by solvent, preheating and post heating temperature, concentration of sol, substrate and procedure of coating. In this work to obtained convenient sol we carried out the reaction at 65 0C for 45 min until revealed clear homogeneous solution. The XRD pattern of the zincite thin film on microscope glass slid by five spin-coating (5-layer) pre-heated at 275°C for 10 min and post-heated for 80 min at different temperature, 350°C, 450°C and 550°C Shown in Fig. 1. We have observed that there are three distinct differences between the XRD results of thin films and powder of binary zincite. Firstly diffraction peaks of thin films have lower intensity and higher FWHM (Fully Width at Half Maximum) compare to powder, secondly, the films are predominantly (002) oriented and finally films are crystallized at comparatively

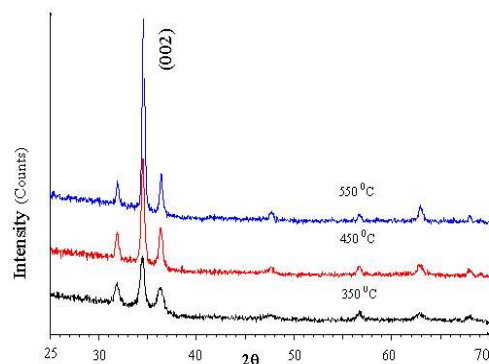


Fig. 1: The XRD pattern of the binary zincite thin films

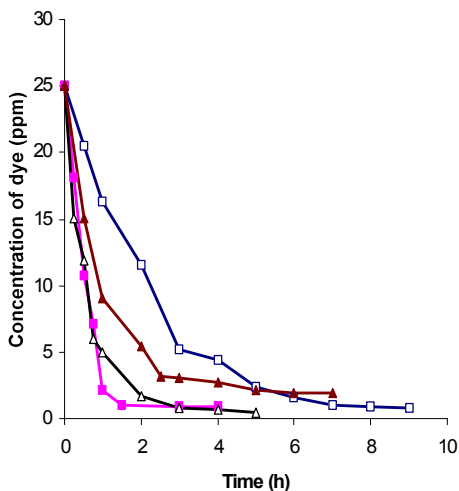


Fig. 2: Concentration of dyes (25ppm), (□) Direct Orange 39, (■) Direct Blue 256, (Δ) Direct Red 81 (▲) Direct Yellow 86 in de-ionized water after photocatalytic decolorization under UV irradiation on granule glass coated with zincite nanostructured film with 5-layer

higher temperature as compared to powder that have prepared from chemical producers. It was observed that increasing temperature of annealing affected the intensity of (002) peak. It can be seen that orientation of thin films is highest at 550°C. The zincite films grow with a (002) orientation because such growth is kinetically preferred, which in turn likely reflects the fact that highest density of Zn atoms is found along the (002) plane [28].

Films were pre-heated at 275°C for 10 min and post-heated at 450°C, for 80 min. The deposition was repeated for 5 times to obtain a film with appropriate thickness. The average grain size of nanostructure binary zincite thin films were about 67 nm.

Photocatalytic activity: Evaluation of the granule glass coated with zincite nanostructured as potential photocatalysts for water pollutant purification was based on the decolorization of dyes. The experiments showed that binary zincite nano on granule glass and UV light (365nm) had a negligible effect when they were used on their own after 4 hours. Fig. 2 shows the decolorization of some dyes (25 ppm) under UV irradiation (365nm) on granule glass coated with zincite nanostructured with 5-layers.

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