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Ultraviolet to visible-light range photocatalytic activity of ZnO films prepared using sol–gel method: The influence of solvent

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ABSTRACT

The textile industry is characterized by high consumption of water, fuel, and chemicals. The wastewater treatment and recycling possibilities in the textile industry are environmentally of the highest importance. The most common chemical pollutants present in textile industry wastewater are the azo-dyes. The solution based sol–gel method was used to synthesize ZnO thin films using different solvents to evaluate the morphology-dependent photocatalytic activity toward the degradation of two azo dyes including sodium [3-[(4,5-dihydro- 3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]-2-hydroxy-5-nitrobenzenesulp-honato (3-)] hydroxychromate (1-) and sodium (5-((4′-(((2,6-dihydroxy-3-((2-hydroxy-5-sulfophenyl)azo)phenyl)azo)-4-biphenylylazo) salicylato (4-)) cuprate (2-) in water. 2-Propanol, methanol, ethanol, and 1,4-butanediol were used as solvents. The photocatalytic degradation rates depend on the dye structure and concentration, solvent-dependent ZnO film morphologies, pH of the medium and excitation light source. The observed rate constants of ZnO film prepared using 2-propanol and of ZnO film prepared using methanol were enhanced approximately by a factor of 3 under UV light and under visible light, respectively. The obtained results were discussed according to the structure and morphology of ZnO films as key parameters in photocatalytic activity.

1. Introduction

The reuse and recycling of wastewater effluent are rapidly growing and becoming a necessity for water utilities to enhance limited fresh water supply, which is currently under pressure due to rapid population growth [1]. The health of ecosystem and drinking water supplies can be directly impacted due to the presence of toxic organic compounds such as dyes in wastewater, their variety, toxicity, and persistence [2]. Among the synthetic dyes, which are widely used for textile dyeing and other industrial applications and are released in large quantities into the environment, those containing an azo chromophore constitute the largest class [3]. Azo dyes are recalcitrant to microbial degradation, causing problems in the usual biological treatment of the industrial effluents [4].

Heterogeneous photocatalysis by irradiating a metal oxide semiconductor has been considered as a cost-effective alternative as pre- or post-treatment of the biological treatment process for the purification of dye-containing wastewater. However, the use of artificial UV light for photodegradation purposes is expensive due to the requirement of the additional power supply. So, there are limitations for the use of metal oxide semiconductor in the treatment of wastewater using UV light from practical point of view. Recently, most of the investigations have focused on preparing catalysts which can be activated by visible light due to the more available energy provided by the sunlight.

Understanding the impacts of various process parameters that govern the photocatalytic degradation efficiency is of paramount importance from the design and the operational points of view to choose a sustainable, efficient technique for the treatment of wastewater. Nanostructured materials offer promising opportunities for improved and tailored properties for application in environmental catalysis due to their unique physicochemical properties, caused by their nanosized dimensions and large surface/volume ratios [5,6]. The synthesis of nearly all kinds of nanostructured materials, including metals, metal oxides, and semiconductors, has now been realized. However, there are still two main challenges remaining in this field, rationally controlled synthesis and large scale production. Since controlling the crystal planes of nanomaterials is a paramount target in catalyst preparation, what must follow is the “design” rather than the “preparation” of nanocatalysts. The ideal way is to first fully understand the relationship between crystal structure and corresponding catalytic properties, and then to synthesize nanocatalysts with well-defined reactive crystal planes [7–12]. Hence, it is very desirable to synthesize nanocatalysts with high ratios of more reactive crystal planes. Unfortunately, surfaces with high reactivity usually diminish

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rapidly during the crystal growth process as a result of the minimization of surface energy because the planes with higher surface energy are more reactive [13].

Among metal oxide semiconductors, although TiO_2 remains the most utilized photocatalyst in both water and air decontamination, ZnO is increasingly recognized as a suitable alternative due to its comparable band gap energy (3.37 eV) and relatively lower cost of production [14,15]. ZnO was also reported to exhibit higher quantum efficiency and photocatalytic activity than TiO_2 in certain cases [16–20]. It is also well known that ZnO exhibits the richest range of morphologies among the wide band gap semiconductors. Solid templates or structure-directing agents are commonly used to fabricate materials with hierarchical structures [21,22], but impurities can be introduced from the templates or agents that can affect the properties adversely. There is, therefore, significant interest in developing facile, template-free, solution-based, morphology controlled approaches to building the self-generated architectures. Currently, ZnO is an interesting nanoparticle semiconductor material, especially because of its application in photoassisted reactions in the process of reduction or elimination of water contaminants, and the self-cleaning (anti-bacterial) [23–27]. The synthesis of nanostructured ZnO with a high surface area and a controlled and stable phase composition, with the aim of reaching higher photocatalytic activity closer to the visible region is mainly focused on its textural and morphological properties [28–34].

Most of the studies related to photodegradation reactions have been carried out using suspensions of powdered ZnO in aqueous solutions [35–37]. However the two major limitations for its wide practical application are the relative small percentage of photons of the solar radiation, which has the required energy to photogenerate electrons and holes, and their high charge recombination rate. Another practical limitation is the photocatalyst removal; its removal from water is difficult and therefore recent research has focused on the preparation of highly photoactive immobilized catalysts for water treatment [38,39]. There are some recent studies that show that the activity of ZnO could be unaffected under certain conditions when it is immobilized [40–42].

It is well known that the preparation parameters in the synthesis of any catalyst are determinant in the final properties of the material [43–47]. A wet-chemical method could be employed to prepare zinc oxide nanocrystals having controlled morphology through using zinc precursor in solvent under mild conditions. This solution method offers finer tailoring of the size and shape of the nanocrystals and is complementary to most reported physical methods. Among solution-based methods, sol–gel process has many advantages such as an easier composition control, better homogeneity, low processing temperature, lower cost, easier fabrication of large area films, possibility of using high purity starting materials and having an easy coating process of large and complex shaped substrates [48]. Several parameters including precursor nature and concentration, solvent nature and hydrolysis ratio, presence and nature of catalysts, as well as aging time and temperature influence the structure and properties of sol–gel derived materials over a wide range [49–52].

Since the solvent physico-chemical properties such as polarity, viscosity, and softness will strongly influence the solubility and transport behavior of the precursors, the solvent in a sol–gel process could be used as shape/or size-controller of nanocrystallites. The control of stable crystalline size and phase obtained by the sol–gel method is one of the most versatile, reproducible procedures to obtain high reactivity, small crystallites and large surface areas [53,54]. These peculiarities, together with the mild synthesis conditions (soft chemistry), make the sol–gel method particularly suitable for yielding nanosystems with suitable control over chemical composition, morphology, and microstructure. It was found that the crystallite growth habits and sizes of ZnO nanocrystallites could be controlled by changing the solvent during the solvothermal synthesis [55–58], but however, not many studies have been carried out concerning solvent nature influencing the structure and properties of sol–gel derived materials especially photocatalytic activity [59–63].

This paper describes the preparation of ZnO supported on non-seeded substrate, employing a simple and environmentally benign method based on the sol–gel hydrolysis of zinc acetate, as raw material which is inexpensive, and easy to handle. Visible light activity has been usually induced in ZnO by surface modification via organic materials/semiconductor coupling and band gap modification by doping with metals and nonmetals, co-doping with nonmetals, creation of oxygen vacancies and oxygen sub-stoichiometry. However, in our work, the desired characteristics were attained through the change and control of the solvents with the aim of evaluation in photoresponsive properties and photocatalytic efficiency in ultraviolet to visible-light range.

2. Experimental section

2.1. Synthesis of ZnO thin films

All reagents were analytical grade. Zinc acetate dihydrate $Zn(COOCH_3)_2 \cdot 2H_2O$ as the starting salt material and ethanol, methanol, 1,4-butanediol, and 2-propanol were used as solvents to prepare ZnO thin films by sol–gel method. Table 1 shows some physical features of used solvents. In a typical sol–gel synthesis of ZnO, zinc acetate was first dissolved in solvent: monoethanolamine (MEA) solution with 1:1 molar ratio at room temperature. Since zinc acetate has low solubility in selected solvents, MEA was added to obtain a transparent solution and to keep the solution stable. The mixture was stirred by stirring at 60 °C until a clear and homogeneous solution formed. The precursor solution prepared did not produce any precipitates after 5 weeks of storage. The microscope glass substrates were cleaned with dilute HCl solution and distilled water. The thin films were coated on glass by the dip coating process. The substrate withdrawal speed was 20–25 mm/min and the coated substrate was heated at 190 °C in an oven for 20 min. By repeating the process five times, ZnO films with desired thickness were obtained and then the final coating annealed in a furnace in air at 550 °C under ambient pressure for 1 h. After here for convenience, the prepared ZnO films using 2-propanol, methanol, ethanol and 1,4-butandiol as solvent refer as ZnO-P, ZnO-M, ZnO-E and ZnO-B, respectively.

2.2. Characterization

To characterize the ZnO thin films, X-ray power diffraction (XRD) experiments were performed on a Bruker, D8 ADVANCEXRD diffraction spectrometer with a Cu Kα line at 1.5406 Å and a Ni filter for an angle range of $2\theta = 20–80°$. Philips, XL30 scanning electron microscope (SEM) measurements were also used to investigate the morphology of the samples with an accelerating voltage of 17 kV. The optical properties were performed on a Shimadzu, MPC-2200 UV–vis spectrophotometer operated over the range of 350–600 nm at a resolution of 2.0 nm. N_2 physisorption was performed in an A-series BEL SORP 18 nitrogen adsorption apparatus to study surface area of the ZnO samples.

Table 1
Physical features of the ZnO films synthesized via a sol–gel process using different alcohols as solvent.

Solvent	Dielectric constant	Viscosity (25 °C) (cP)	ZnO films			
			Crystal size (nm)		Photon energy, hυ (E_g, eV)	(100)/(002) intensity ratio
			SEM	XRD		
2-Propanol	19.25	2.4	49	38	3.09	1.18
Methanol	33.6	0.59	52	40	3.07	0.76
Ethanol	24.3	1.1	64	73	3.18	0.64
1,4-butanediol	31.9	7.1	78	83	3.22	0.07

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