Materials Science in Semiconductor Processing 26 (2014) 603–613

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Photodegradation of phenol by zinc oxide, titania and zinc oxide–titania composites: Nanoparticle synthesis, characterization and comparative photocatalytic efficiencies

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ARTICLE INFO

Available online 14 June 2014

Keywords:
Nanoparticles
ZnO–TiO_2nanocomposite particles
Photocatalytic degradation
Phenol

ABSTRACT

Nano-ZnO, TiO_2 and ZnO–TiO_2 composite particles were synthesized by a sol–gel method and were used as catalysts in the photocatalytic degradation. The nanocatalysts were characterized by XRD, SEM, EDX and BET methods. The experimental results showed that the nano-ZnO particles are large agglomerates having a hexagonal wurtzite structure of particle size 17.5 ± 5 nm, nano-TiO_2 has uniform particles size of 15 ± 5 nm with spherical morphology. The nano-ZnO–TiO_2 composite particles are of large agglomerates being embedded inside with particle size of 11.6 ± 5 nm. The photocatalytic activity of nano-ZnO, TiO_2 and ZnO–TiO_2 composite particles was evaluated using phenol as a model compound. The effect of initial pH, initial catalyst loading and concentration of phenol under UV light irradiation and direct sun light was studied. The photodegradation of phenol was found to follow pseudo-first order kinetics and the experimental results proved that the nano-ZnO, TiO_2 and ZnO–TiO_2 composite particles are efficient catalysts for phenol degradation in the presence of UV light. Total organic carbon analysis indicated complete mineralization of phenol in the presence of nano-ZnO, TiO_2 and ZnO–TiO_2 surface.

1. Introduction

Hazardous organic compounds generated from industries involved in plating, machining, cosmetic production, food processing, textile processing, and also from paint, pesticide, coal conversion, polymeric resin, petroleum and petrochemical industries are discharged into wastewaters. They are the major cause of environmental pollution. Among the pollutants, phenols are generally considered to be one of the most important toxic organic pollutants which when released into the environment causes unpleasant taste and odor to ground and surface waters. The waters polluted with phenol and its derivatives are difficult to treat and are well known for their bio recalcitrant and acute toxicity [1]. Phenol is a toxic and mutagenic substance at high concentrations and may be absorbed through skin [2]. Hence there is a need to develop effective treatment methods to eliminate organic contaminants from wastewaters by conventional chemical treatment systems. Traditional wastewater treatment methods are partly effective, non-destructive, inefficient, costly or just transfers pollutants from water to another phase as secondary pollutant [3]. In pursuit of a better method for the treatment of wastewater, heterogeneous photocatalysis stands superior [4]. The important advantage of this degradation method is that it can be carried out under ambient conditions and results in complete mineralization of the organic contaminants.

Heterogeneous catalysis using ZnO, TiO_2, WO_3, SnO_2, ZrO_2, CeO_2, CdS and ZnS as catalysts in the presence of UV or solar light is used to achieve mineralization of toxic pollutants present in wastewater [5]. Among them, nano-ZnO and TiO_2 have been dominating among the photocatalysts [6]. One of

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http://dx.doi.org/10.1016/j.mssp.2014.05.031
1369-8001/

the major applications of heterogeneous catalysis is photocatalytic oxidation (PCO) or to affect total mineralization of gas phase or liquid phase contaminants into benign substances like CO_2, H_2O, NO_3^-, PO_4^{3-} and halide ions [7]. Nanostructured ZnO and TiO_2 have been prepared and tested as effective catalysts in the degradation of organic targets activated by light and have higher photocatalytic efficiency than their commercial counterpart. ZnO, one of the most important multifunctional semiconductor materials, is attractive for its unique performance in electronics, optics and photonics because of its wide direct band gap of 3.37 eV and high excitation binding energy of 60 meV [8]. It is an exceptionally important material for applications in photo-catalysis, antibacterial materials, sensors and dye sensitized solar cells due to its excellent optical, electrical, mechanical and chemical properties [9].

Nano-TiO_2 photocatalyst has attracted interest in recent years for its highly active photocatalytic functions, such as the ability to decompose chemical compounds and for its super hydrophilic and antibacterial properties. Nano-TiO_2 is most popular as a heterogeneous photocatalyst among the semiconductors due to its excellent optical and electronic properties, low cost, non-toxicity, chemical and thermal stability [10]. Nano-ZnO is sometimes preferred over TiO_2 for the degradation of organic pollutants due to its high quantum efficiency [11]. However, it photocorrodes in acidic aqueous suspensions [12]. Under UV light irradiation, both TiO_2 and ZnO nanoparticles are highly efficient photocatalysts since their photogenerated electrons and holes are highly oxidizing and reducing agents respectively. In addition, coupled semiconductor photocatalysts provide an interesting way to increase the efficiency of a photocatalytic process by increasing charge separation and extending the energy range of photoexcitation for the system. ZnO–TiO_2 nanocomposite particles have been used as a promising photocatalyst in the degradation of organics [13]. In the countries where sufficient amount of sunlight is available, photocatalysis involving sunlight will be economical and preferable. Therefore, there is a need to develop effective photocatalysts which can be used for the photocatalytic degradation of organic pollutants in the presence of sunlight.

The present study involves the synthesis of ZnO, TiO_2 and ZnO–TiO_2 composite nanoparticles by sol–gel method and their characterization by XRD, SEM, EDX and BET methods. The photocatalytic activity of nano-ZnO, TiO_2 and ZnO–TiO_2 composite particles is investigated using phenol as a model compound. Photocatalytic degradation of phenol was carried out by irradiating UV light and in the presence of sun light. The effect of initial pH, initial catalyst loading and concentration of phenol in the presence of UV light and sunlight on nano-ZnO and TiO_2 surfaces was investigated. Kinetic studies of photocatalytic degradation of phenol by nano-ZnO, TiO_2 and ZnO–TiO_2 composite particles were also attempted.

2. Experimental and analytical

2.1. Materials and methods

Zinc acetate dihydrate, oxalic acid dihydrate, ethanol, titanium (IV) isopropoxide, glacial acetic acid, diethanolamine and phenol were of analytical grade purchased from Merck, SRL, Qualigens. Double distilled water was used for all the measurements. The estimation of phenol was carried out spectrophotometrically using a 4-aminoantipyrene method [14].

2.2. Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized by a sol–gel method. In this procedure, 5.49 g of zinc acetate dihydrate was mixed with 150 ml of ethanol in a rotary evaporator at 60 °C and fixed the rotation at 40 rpm. The zinc salt was completely dissolved in 10–15 min. Simultaneously, 6.3 g of oxalic acid dihydrate was dissolved in 100 ml of ethanol by stirring for 10 min at 50 °C using a magnetic stirrer. To the oxalic acid solution, the warm ethanolic solution of zinc acetate was added dropwise with continuous stirring. Stirring was continued for another 45 min after complete addition of zinc acetate solution. A thick white gel of zinc oxide was obtained which was dried in a vacuum oven at 80 °C for 20 h to get xerogel. The xerogel was then calcined at 500 °C in a tubular furnace at a ramp rate of 3 °C/min for 5 h to yield ZnO nanoparticles.

2.3. Synthesis of TiO_2 nanoparticles

In the sol–gel method of synthesis of TiO_2 titanium (IV) isopropoxide, glacial acetic acid and double distilled water were used in a molar ratio of 1:10:350. 18.6 ml of titanium (IV) isopropoxide was hydrolyzed by slowly adding 35.8 ml of glacial acetic acid with constant and vigorous stirring at 0 °C. To this solution, 395 ml of double distilled water was added dropwise under vigorous stirring for 1 h and then continued stirring for 3 h. The prepared titania solution was ultrasonicated for 30 min until a clear solution was formed. The solution was kept undisturbed for 24 h in dark for a nucleation process. It was then gelated in an oven at 70 °C for 12 h to get the xerogel of titania. The titania gel was kept in an oven at 100 °C for its complete dryness. The resulting TiO_2 sample was crushed into very fine powder and was then calcined in a muffle furnace at 500 °C for 5 h to get TiO_2 nanoparticles.

2.4. Synthesis of nano-ZnO–TiO_2 composite particles

The synthesis of nano-ZnO–TiO_2 composite was also carried out by the sol–gel method. The titanium (IV) isopropoxide was used as a precursor material to synthesize transparent TiO_2 sol. 4.32 ml of titanium (IV) isopropoxide was dissolved in 20 ml of ethanol and stirred for half an hour using a magnetic stirrer with medium rotation to get a titania precursor solution. A mixture of 0.26 ml of distilled water, 3.4 ml of glacial acetic acid and 5 ml of ethanol was then added dropwise into the precursor solution at a speed of one drop per second under continuous stirring. The solution was then continuously stirred for $\sim$1 h to achieve a yellow transparent sol. The sol was then aged for a period of time. Here, glacial acetic acid was used as an inhibitor to slow down the titanium (IV) isopropoxide hydrolysis. In this case, the pH of the system was determined to be $\sim$5 and hence the obtained sol is referred to as an acidic sol. On the other hand, another inhibitor of diethanolamine was used