Materials Science in Semiconductor Processing 31 (2015) 315–324

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Study on photocatalytic activity of ZnO nanoneedles, nanorods, pyramids and hierarchical structures obtained by spray pyrolysis method

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ARTICLE INFO

Available online 24 December 2014

Keywords:
Zinc oxide
Hierarchical
Spray pyrolysis
Photocatalytic activity

ABSTRACT

In this research, ZnO nanostructured layers with various morphology, i.e. nanoneedles, nanorods, pyramid shaped ZnO crystals, and hierarchical structures of ZnO deposited on nanorods and pyramid shaped crystals, were synthesised by pneumatic spray pyrolysis method. Hierarchical structures, a dense network of well-ordered platelets covering the side facets of the rod-like and pyramid shaped ZnO crystals, were obtained by spraying Zn $(Ac)_2$ solution over the surface of pre-grown ZnO crystals at deposition temperature of 330 °C within 5 min. All ZnO layers have been characterised by scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), absorbance of ultraviolet and visible light (UV–vis), surface wettability measurements and photoluminescence (PL). Photocatalytic activity of the layers was evaluated by means of photocatalytic oxidation activity (PCO) of several organic pollutants, namely, methyl-tert-butyl ether (MTBE), humic acid (HA), N,N-dimethyl p-nitrosoaniline (RNO), and prednisolone (PNL); the results were compared to the performance of well-established commercial photocatalyst, P25 titanium dioxide (Evonik). MTBE was the most efficiently degradable compound by all objects, while RNO was effectively degraded by plain structures only. In HA photocatalysis, needle-like ZnO as the most efficient material; PNL was the least degradable by ZnO layers. In the degradation of MTBE, RNO and HA, ZnO objects have shown activity comparable to or highly exceeding that of P25 TiO_2. The explanation of the differences in ZnO objects' photoactivity is proposed to be the different character of oxidising species produced by the ZnO objects, and different interactions of these with the degradation substrates, based on the relative amount of surface defects, surface morphology and hydroxylation of the ZnO structures' surface.

1. Introduction

The interest in the preparation of ZnO nanostructures such as nanowires, nanorods, hierarchical structures of ZnO is continuously growing due to the wide potential of their applications in optoelectronic devices, gas sensors, or

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http://dx.doi.org/10.1016/j.mssp.2014.12.012
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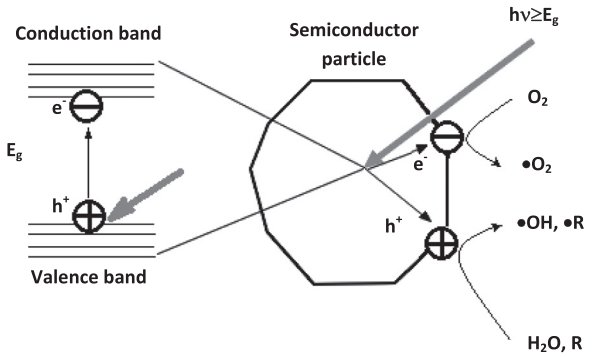

Fig. 1. Schematic representation of photocatalytic oxidation working principle: $h\nu$ stands for electromagnetic radiation, E_g for band gap, e^- for electron and h^+ for hole.

photocatalysis for degradation of environmentally hazardous pollutants. For photocatalysis ZnO has been attracted great interest due to its low cost, low-toxicity, abundancy, and ease of preparation of ZnO with various morphologies.

Up to now there are many reports on efficient photocatalytic activity of ZnO nanorods and hierarchical structures deposited by electrodeposition, chemical bath, solvothermal method [1,2].

In addition to these techniques, spray pyrolysis is a very simple and relatively low-cost processing method for preparing plain and nanostructured layers with precise composition control, precise stoichiometry, high crystallinity and purity of the materials [3–5]. In spite of many reports on photocatalytic activity of the ZnO layers it is still a great challenge to produce photocatalitically active ZnO with new morphologies by inexpensive and well controllable techniques and study their photocatalitical properties with respect to the growth conditions.

Herein, we present a study on synthesis and photocatalytic performance of spray-deposited ZnO nanostructured layers with various morphology, namely, nanoneedles, rods, hierarchical structures grown on the rods, pyramid shaped crystals, and hierarchical structures grown on the pyramid shaped crystals.

Literature data on various ZnO objects (including hierarchical ones) synthesis and activity testing is plentiful, but it deals mostly with dyes as degradation substrates, such as methyl orange (MO) [2,6,7], methylene blue (MB) [8–10], rezaurin [11], rhodamine B (RhB) [1], etc., in mg L^{-1} scale, with degradation rates ranging from 40% to 100%; some notable exceptions are the works dealing with degradation of actual pollutants, such as 2,4-dichlorophenoxyacetic acid (2,4-D) [12], estrone [13] and 4-chlorophenol (4-CP) [14]; as a rule, only one degradation substrate is used in such works. The authors' approach, on the other hand, lies within assessment of their objects' photocatalytic activity by degrading several organic pollutant types with different structure, giving a more detailed insight on their abilities.

In order to assess the photoactivity of ZnO layers, the authors chose aqueous photocatalytic oxidation of several organic compounds with different structure. Photocatalytic oxidation is a phenomenon based on the creation of excitons by the subjection of the semiconductor material to electromagnetic radiation the quanta of which possess equal or higher energy to that of the semiconductor's band gap. With the existence of suitable charge carrier traps (e.g. oxygen vacancies, surface defects, sharp edges, etc.), positively charged holes produce hydroxyl radicals from water molecules, or can directly substract pollutant molecules' electrons. At the same time, conduction band electrons reduce suitable electron acceptors (e.g. dissolved oxygen). This way, the defects on irradiated semiconductor material are a source of reactive oxygen species (ROS). Besides the relative abundance of defects, their availability to the aqueous pollutant (governed both geometrically and hydrodynamically by the surface morphology) and chemical composition of the surface (hydroxylated surfaces produce hydroxyl radicals, while non-hydroxylated ones produce less potent oxidising species) are the primary factors influencing the photocatalytic oxidation efficiency. The mechanism of photocatalysis is schematically represented in Fig. 1.

The following compounds were chosen to evaluate the photocatalytic activity of ZnO objects in this study: methyl-tert-butyl ether (MTBE, CAS 1634-04-4), humic acid sodium salt (HA, CAS 68131-04-4), N,N-dimethyl p-nitrosoaniline (RNO, CAS 138-89-6) and prednisolone (PNL, CAS 50-24-8). An aliphatic and relatively non-polar MTBE is perhaps best known as a fuel additive, used worldwide, although banned for some time in the United States; it is non-biodegradable and hard to remove from water by conventional means, and a suspected carcinogen [15–18]. RNO is an aromatic compound, which has also seen the application in measuring the number of hydroxyl radicals in various advanced oxidation processes (AOPs), including photocatalysis, due to RNO decolouration upon stoichiometric reaction of its molecule with OH-radical [19]. Humic acid was chosen as a representative of a wider compound class, humic substances (HS), the product of plant matter decay, that have various polycyclic, aromatic and heteroatom-containing functional groups; besides the coloration of water, HS, being radical scavengers and thus hardly affected by common water treatment methods, are easily bonded with heavy metals and other toxics [20], being able to effectively transport them through drinking water treatment stages [21]. Upon HS-containing water chlorination, they serve as a source of carcinogenic trihalomethanes [22,23]. Finally, PNL is a widely used glucocorticoid anti-inflammatory agent, and as such is a very common emerging micropollutant [24]. The substances' structural formulae can be seen in Fig. 2.

The aim of this study was the synthesis and investigation of hierarchical ZnO objects, possessing different morphology and surface properties, and thorough and representative investigation of their photoactivity by their action on several substrates with different chemical structure and properties. Such an approach will no doubt give an objective view on the new materials and their abilities in the light of their possible applications. This should give an insight on the characteristics of an “ideal” photocatalytic material in terms of its structure and properties, and, consequently, on the conditions of synthesis which would provide such a material.