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Photocatalytic degradation behavior of multiple xenobiotics using MOCVD synthesized ZnO nanowires

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ABSTRACT

In this study, we investigated the beneficial properties of ZnO nanowires grown via a MOCVD (Metal Organic Chemical Vapor Deposition) process for the photocatalytic treatment of a solution containing seven xenobiotics that are commonly found in waste or surface water. A physicochemical characterization of the ZnO nanowires was performed to highlight the advantages of the high-temperature gas-phase MOCVD process for the synthesis of photocatalytic ZnO materials. In addition, the photocatalytic degradation of carbamazepine, diclofenac, lidocaine, metoprolol, propranolol, sulfadimidine and atenolol was studied for the first time using a one-step experiment under a low power 365 nm UV light (2.28 mW cm^{-2}). We determined the fast photodegradation kinetics of all of the xenobiotics present in the solution. These results support the use of photocatalytic methods for the removal and degradation of xenobiotics.

1. Introduction

Water is an essential resource for life and a key factor for socio-economic development. The unbridled use of water is a global problem that has resulted in major environmental and social challenges. Moreover, global climate change will certainly impact freshwater resources, and the projections of the water cycle changes remain unclear. Water is at the intersection of climate change and life, and environmental concerns require our attention and suggest that we should not abuse the use of water. *Abusus non tollitusum — the abuse does not exclude the use or let us use but not abuse*. The purification of wastewater via the elimination of toxic pollutants, such as xenobiotics, from wastewater represents an increasing concern in our society with regard to drinking water, wastewater and water reuse treatment systems [1].

The important sources of pollutants in wastewater and aquatic ecosystems typically originate from industrial applications (i.e., petroleum refining, textile processing, sewage effluents or from household and personal care areas, runoff from agriculture, pesticides and fertilizers, landfill leachates, detergents, livestock and aquaculture, flame retardants, pharmaceuticals, hormones, hospital waste, animal excrement, and improper disposal of unused pharmaceuticals) [2–4]. Among these pollutants, pharmaceutical compounds are among the most abundant in the aquatic environment. Wastewater from pharmaceutical industries and households contains drugs, including endocrine disruptor compounds, illicit drugs, anticancer drugs, steroids, antidepressants, analgesics, anti-inflammatory agents, antipyretics, beta-blockers, lipid-lowering drugs, tranquilizers, stimulants, and antibiotics [5]. These pharmaceutical compounds are highly polar with low volatility and can enter the aquatic environment or remain adsorbed on solid particles via electrostatic forces, which prevents their separation or degradation via a biological treatment process [6], or conventional urban water treatment method. In general, wastewater treatment plants are designed to treat easily or moderately biodegradable compounds but not pharmaceutical compounds [7]. Therefore, these xenobiotics may remain in the environment for a long period of time and their elimination from water can be complicated, which may result a potential toxic effects on the ecosystem or even on human health [8]. Although some pharmaceutical compounds can be eliminated via various processes, such as dilution, photolysis or biodegradation [9], pharmaceuticals are designed to be metabolically resistant and active at low concentrations [10]. Trace concentrations of pharmaceuticals are a known health risk to humans and to terrestrial and aquatic ecosystems. These compounds may have a physiological effect on humans and animals (vertebrates and invertebrates) [11] and on the ecosystem as a

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whole [12,13]. The effects on the aquatic ecosystem may include loss of habitat and biodiversity, feminization of fish and development of microbiological resistance and accumulation in soil, plants and animals [14–16]. However, insight into the long-term risks to non-target organisms and human health remains unclear [17], and in this context, significant research efforts focused on wastewater treatment are needed to develop effective technologies for xenobiotic removal. Therefore, the threats to the aquatic life and all living beings due to pharmaceutical drugs have motivated recent studies [18–20].

The stable xenobiotics found in surface water include beta blockers, such as propranolol, metoprolol or atenolol [21,22], neuroactive compounds, such as carbamazepine [21], anti-inflammatory agents, such as diclofenac[23], antibacterial agents, such as sulfadimidine [7], or anesthetics, such as lidocaine [8]. A sample of water from the Luxembourgish river (i.e., Alzette) was tested, which revealed the presence of all of the listed molecules. For the xenobiotics that remain after biological degradation in a wastewater treatment plant, different strategies must be developed for their elimination. Filtration processes using membranes [26], or stabilization on a soil filter [27] are two current processes that are employed to clean water. However, some pollutants are not completely eliminated. In addition, the post treatment of the membranes or soil is necessary. Other abiotic processes are employed in photolytic advanced oxidations [28]. In the environment, the xenobiotics may be susceptible to degradation upon exposure to solar radiation [2]. Although the toxic effects of the degradation byproducts as well as the degradation mechanism remain unclear, many studies have focuses on the photolytic degradation of drugs present in wastewater [29]. Photolytic processes rely on the generation of hydroxyl radicals (OH·) in water under UV irradiation. The as-formed OH · have an oxidation-reduction potential that is sufficient to oxidize nearly any organic compound present in water, leading to their degradation. To achieve rapid decomposition of dilute organic matter in water, photolytic processes typically require the use of high power UV lamps [30,31], and are often associated with OH· radical generators, such as hydrogen peroxide [32]. Although photolytic processes are attractive due to their performance, these processes are expensive and energy intensive on a large scale. An environmentally friendly and economic alternative to classic photolytic processes may involve the use of heterogeneous photocatalysis. Heterogeneous photocatalysis refers to the use of photocatalytic materials to generate OH· upon irradiation by an energetic light source. In these processes, the oxidative decomposition of organic molecules occurs at the surface of the photocatalyst. Semiconductors, such as TiO_2 [33], ZnO [34], Fe_3O_4 [35], or SnO_2 [36], are the most studied photocatalytic materials due to their intrinsic properties. If TiO_2 is often considered has the most suitable material for photocatalytic applications, ZnO has the advantage of having a direct electronic band gap of approximately 3.2 eV, an exciton binding energy of approximately 60 meV [37] (4 meV for TiO_2), and can be to synthesized easily in many different structures, even at low temperature. For the photocatalytic degradation of water pollutant or chlorinated compounds (like xenobiotics such as diclofenac), ZnO has been proven to be a better photocatalyst than TiO_2 [38,39]. ZnO is relatively stable, biocompatible and readily available. Therefore, it appears as a promising candidate for the photocatalytic degradation of complex organics in water. In addition, it is also a potential material for use in solar cells, photodiodes, piezoelectric or nanogenerators [40].

ZnO can be synthesized using many different techniques in the liquid or dry phase. Liquid-phase processes are typically associated with low temperature syntheses including hydrothermal [41], solvothermal [42], sol-gel [43], or precipitation processes [44]. The low temperature in these synthesis techniques often leads to the presence of defects or impurities in ZnO [45]. Dry synthesis processes (i.e., chemical vapor deposition (CVD) [46] or physical vapor deposition (PVD)) are typically employed at high temperatures and low pressures [47]. In general, CVD processes result in highly crystalline ZnO structures with low defect concentrations [48]. Therefore, these processes are important for the synthesis of high quality ZnO structures on non-thermosensitive substrates, such as silicon wafers.

The photocatalytic performances of ZnO nanostructures, such as nanofilms, nanoparticles or nanowires, have been extensively investigated [34,49–51]. ZnO nanocomposites such as Pt-ZnO [52,53], WO_3-ZnO [54], ZnO/C/Fe_3O_4 [55], or Mo-doped ZnO [56] were proposed to improve the photocatalytic performances of ZnO nanoparticles by preventing the electron/hole recombination, or by activating ZnO in the visible light range. However, most of these studies focus only on the photocatalytic treatment of solutions containing only one pollutant, such as dyes like methylene blue, acid orange II, methyl orange, Rhodamine B or drugs like tetracycline [57] or ciprofloxacin [58].

In this study, we investigated the photocatalytic behavior of ZnO nanowires grown by MOCVD for the photocatalytic treatment of a solution containing multiple xenobiotics (i.e., propranolol, metoprolol, atenolol, carbamazepine, diclofenac, sulfadimidine and lidocaine). The performances of ZnO nanowire photocatalysts for the one-step treatment of a solution containing seven xenobiotics that are commonly found in surface water are determined.

2. Experimental section

2.1. Chemicals

The chemicals used to synthesize the ZnO nanowires and perform the photocatalytic degradation test were purchased from Sigma-Aldrich. These chemicals were used without any additional purification. The studied xenobiotics included propranolol (propranolol hydrochloride ≥ 99%), metoprolol (metoprolol tartrate salt ≥ 98.5%), atenolol (≥98%), carbamazepine (99%), diclofenac (diclofenac sodium salt ≥ 98.5%), sulfadimidine (sulfamethazine sodium salt ≥ 98%) and lidocaine (lidocaine hydrochloride monohydrate solid). The ultrapure water that was used in our study was obtained from a Milli-Q Millipore system (Milli-Q plus 185). The substrate, which was high-purity single side polished (100) silicon wafers that were 4 in. in diameter, was obtained from Sigma-Aldrich. The gases (i.e., oxygen (> 99.5%) and nitrogen (> 99.5%)) were purchased from Air Liquid.

2.2. Synthesis of ZnO nanowires

For the MOCVD synthesis of ZnO, a solution of diethyl zinc (DEZ) with a concentration of 0.1 mol l^{-1} in heptane was used as the zinc source, and oxygen (99%) was used as the oxidant. The reaction was performed in a MC 200 MOCVD reactor from ANNEALSYS. The reaction parameters required to grow ZnO nanowires were as follows: a temperature between 500 and 600 °C, a total pressure in the reactor of less than 5 mBar, a partial pressure of DEZ and Oxygen of 0.01 mBar and 0.097 mBar, respectively, and a partial pressure of nitrogen (i.e., used as carrier gas) of 2.85 mBar. The reaction time was fixed at 2 h.

2.3. Physicochemical characterization techniques

High-resolution scanning electron microscopy (SEM) was performed on a Helios Nanolab 650 microscope from the FEI Company to characterize the morphology of the surface of the ZnO nanowires. The working acceleration voltage was fixed at 2 kV with a current of 25 mA and a working distance of 2.6–8 mm with a resolution up to 1 nm. The chemical compositions of the photocatalysts (i.e., weight percentage, average of five measurements at different points on the solid) were measured by energy-dispersive X-ray (EDX) spectroscopy. The crystallographic/crystalline structures were analyzed using an X-ray powder diffractometer (D8 Discover diffractometer, Bruker, USA) using a CuKα radiation source (λ = 0.1542 nm) and a graphite monochromator. The diffraction patterns were collected under ambient conditions over a range of 20–60° (2 theta). The data were recorded using a 0.02° step size and 2 s at each step. The phases were identified by comparison of