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Effect of annealing temperature on structural and optical properties of Mg-doped ZnO nanoparticles and their photocatalytic efficiency in alprazolam degradation

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Abstract

Mg-doped ZnO nanocrystallites were prepared via conventional solid-state reaction when ZnO and MgO precursors were stoichiometrically mixed and heated at 700 °C, 900 °C and 1100 °C for 2 h in air atmosphere. Influence of annealing temperature on structural and optical properties of the obtained nanoparticles was investigated using X-ray diffraction, scanning electron microscopy, mercury intrusion porosimetry, Raman and UV–vis spectroscopy. The efficiency of Mg-doped ZnO water suspensions in the photocatalytic degradation of alprazolam, short-acting anxiolytic of the benzodiazepine class of psychoactive drugs, under UV irradiation was compared with efficiency of pure ZnO and TiO_2 Degussa P25.

Keywords: A. Powders: solid state reaction; B. Spectroscopy; D. ZnO; Photodegradation

1. Introduction

Environmentally friendly and inexpensive Mg-doped ZnO material system is being investigated for diverse applications which are mainly related to the band gap widening of ZnO by alloying with MgO. By changing the Mg-content, the direct band gap of the Mg-doped ZnO semiconductor could be adjusted from 3.37 eV to 7.8 eV [1]. Similar ionic radii of Zn^{2+} (0.60 Å) and Mg^{2+} (0.57 Å) enable formation of the solid solution despite the lattice mismatch between ZnO (hexagonal wurtzite: $a=3.25$ Å and $c=5.20$ Å) and MgO (cubic periclase: $a=4.24$ Å) structures. Solubility limit of MgO in ZnO is highly restricted (up to 4 at%) [2] and dependent upon the preparation conditions. Mg-doped ZnO is potentionaly attractive material to use in novel optoelectronic and nanoelectronic devices [1,3] and photocatalytic applications [3,4].

Pharmaceuticals are a large group of chemicals which are consumed in very high quantities throughout the world. These compounds are being introduced into the environment on a continuous basis and its continuous input and persistence to the water system may result in a potential risk for aquatic and terrestrial organisms. Until now, a vast group of pharmaceuticals has been found in the environment: analgetics, antibiotics, antiepileptics, β-blockers, antidepressants, anxiolytics, sedatives and contaceptives [5]. Benzodiazepines are widely consumed psychiatric pharmaceuticals and these compounds act on the central nervous system, having anxiolytic, sedative and hypnotic effects [5]. Calisto et al. investigated the relevance of photodegradation processes on the environmental persistence of four benzodiazepines (oxazepam, diazepam, lorazepam and alprazolam). Benzodiazepines were irradiated under simulated solar irradiation and lorazepam was shown to be quickly photodegradated by direct solar radiation, with a half-life time lower than 1 summer sunny day. Other three benzodiazepines oxazepam, diazepam and alprazolam showed to be highly resistant with half-life times of 4, 7 and 228 summer sunny days respectively [6].

Alprazolam (8-chloro-1-methyl-6-phenyl-4H-[1,2,4]triazole [4,3,-α]-[1,4]-benzodiazepine, CAS no. 28981-97-7, $C_{17}H_{13}ClN_4$,

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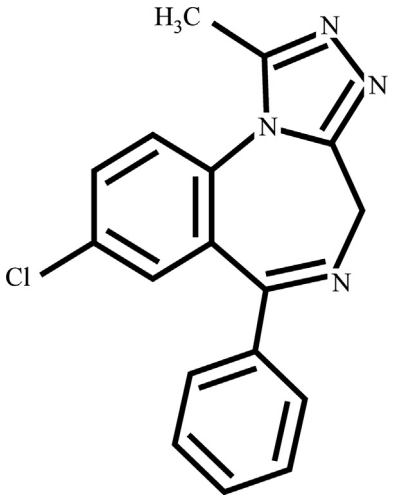

Fig. 1. Structural formula of alprazolam.

M_r=308.765, Fig. 1) is a benzodiazepine derived from 1,4-benzodiazepines of new generation. Alprazolam is extensively prescribed for its therapeutic application such as anxiolytics, anticonvulsant and antidepressant. It is used in the treatment of pathologies that imply anxiety disorders of chronic intensity as the social phobia and other psychosocial pathologies [7,8].

In this work, Mg-doped ZnO powders synthesized via simple solid-state reaction were structurally and optically characterized in an attempt to explain their photocatalytic efficiency differences in degradation of alprazolam. To the best of our knowledge, this is the first study of photocatalytic degradation of alprazolam.

2. Experimental procedures

2.1. Materials and characterization

The Mg-doped ZnO powder samples were obtained when starting ZnO (Sigma-Aldrich, purity 99.9%) and MgO (Centrohem, p.a.) were stoichiometrically mixed to achieve about 5% (w/w) of Mg-doping, in an agate mortar for 10 min and heated in furnace at 700 °C, 900 °C and 1100 °C for 2 h. X-ray diffraction was carried out using a Philips PW 1050 instrument, with Cu $K\alpha_{1,2}$ radiation, and a step scan mode of 0.02°/5 s in angular range 2θ=20–80°. A scanning electron microscope (SEM—JEOL JSM 6460LV) was used to investigate the morphology and microstructure of the samples.

The bulk density measurements were performed on a Macropore Unit 120 (Fisons Instruments). Total mercury intrusion volume (V_{tot}) and specific surface area (SSA) were performed on a Porosimeter 2000 (Fisons Instruments) within the pressure range from 1 to 2000 bar. All samples were dried in an oven at 110 °C during 16 h and additionally evacuated for 90 min at room temperature prior to analysis. Recording of intruded Hg volume vs. applied pressure values was obtained through an interface Milestone 100 Software System for PC. Additionally a Pascal Ver.1.05 software was used for calculation of bulk density (ρ_{bl}), V_{tot} and SSA.

The reflectance spectra were obtained for all samples using an Ocean Optics QE65000 High-sensitivity Fiber Optic Spectrometer, and in accordance with it the Kubelka–Munk function was estimated using a SpectraSuite Ocean Optics operating software. The Raman spectra of the samples were measured using the Centice MMS Raman spectrometer equipped with a CCD detector. A diode laser operating at 785 nm (1.58 eV) with power of 70 mW was used as the excitation source. All measurements were carried out at room temperature.

2.2. Measurements of photocatalytic activity

The photocatalytic activity of the Mg-doped ZnO powders was evaluated by the degradation of the solution of alprazolam (Sigma-Aldrich). The photocatalytic degradation was carried out in a cell described previously [9]. A 125 W high-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335 and 366 nm, with maximum emission at 366 nm), together with an appropriate concave mirror, was used as the radiation source.

Experiments were carried out using 20 mL of 0.03 mmol/L of alprazolam solution and the photocatalyst loading was 1.0 mg/mL. The aqueous suspension was sonicated (50 Hz) in dark for 15 min before illumination, to uniformly disperse the photocatalyst particles and attain adsorption equilibrium. The suspension thus obtained was thermostated at 25 ± 0.5 °C in a stream of O_2 (3.0 mL/min), and then irradiated. During irradiation, the mixture was stirred at a constant rate under continuous O_2 flow. Commercially available TiO_2 Degussa P25 (75% anatase and 25% rutile, specific area of 50 $m^2\,g^{-1}$, and average particle size about 20 nm, according to the producer's specification), was used for the purpose of comparison.

For the HPLC–DAD kinetic studies of alprazolam photodegradation, aliquots of 0.50 mL were taken from the reaction mixture at the beginning of the experiment and at regular time intervals. Aliquot sampling caused a maximum volume variation of ca. 10% in the reaction mixture. The suspensions containing photocatalyst were filtered through a Millipore (Milex-GV, 0.22 μm) membrane filter. After that, a 10-μL sample was injected and analyzed on HPLC—Shimadzu equipped with an Eclypse XDB-C18 column (150 mm × 4.6 mm i.d., particle size 5 μm, 25 °C). The UV/vis DAD detector was set at 222 nm (wavelength of alprazolam maximum absorption). The mobile phase (flow rate 1 mL/min) was a mixture of acetonitrile (ACN, 99.8%, J.T. Baker) and water (40:60, v/v), the water being acidified with 0.1% H_3PO_4 (85%, Sigma-Aldrich).

3. Results and discussion

3.1. Structural and optical characterization

The diffuse reflectance spectra of pure and Mg-doped ZnO powder samples obtained after annealing at 700 °C, 900 °C and 1100 °C were measured to investigate their optical properties.