ACTIVITY EVOLUTION OF NANOCRYSTALLINE ZINC-INDIUM-OXIDE POWDER

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Abstract
In this work, the photocatalytic activity evolution of the mixed zinc-indium-oxide (ZIO) nanocrystalline powders (NCPs) was presented depending on the alterations in its solid-state preparation procedure and different concentrations of the starting precursors. The activity of the obtained ZIO NCPs as photocatalysts was examined through the degradation of two pharmaceutically active compounds (PhACs), the potential organic water pollutants, under simulated solar irradiation (SSI).

Introduction
The presence of PhACs in drinking and environmental waters was found in many countries and mainly this pollution originates from the wastewater treatment plants [1]. Residual traces of PhACs after the usual treatment of the waste and contaminated waters are an increasing pollution problem that needs a prompt solution in the form of the supplementary methods for further purification, like heterogeneous photocatalysis (HPC). HPC is one of the alternative wastewater treatment technologies known as advanced oxidation processes (AOPs) [2, 3]. HPC generally implies the presence of a metal oxide semiconductor in the contaminated waters and simultaneous illumination with either ultraviolet (UV) or even better visible (Vis) light source. Through higher oxidation processes, and the formation of highly reactive oxidizing agents (mainly hydroxyl radicals $^{\bullet}OH$), the organic pollutants in water are transformed over time to less toxic chemicals, inorganic ions, or totally harmless carbon dioxide and water. The efficiency of the metal oxide semiconductor catalyst is measured by the time it takes to degrade the organic substance under the influence of the applied electromagnetic light (UV or Vis). The best efficiency of the photocatalyst is when it takes a shorter time for the organic substance to decompose in the presence of a given photocatalyst, and for the sake of the cost-efficiency if possible under the influence of the sunlight. Zinc-indium-oxide system is a promising candidate that supports the photodegradation of the organic pollutants and could replace the most used material for this application, titanium dioxide (TiO_2) Degussa P25 [4].

Experimental
The mixtures of ZIO NCPs were prepared using the environmentally friendly solid-state method. Starting precursors were commercial zinc oxide (ZnO) and indium oxide (In_2O_3) powders purchased from Sigma-Aldrich (purity 99.9%). The preparatory procedure varied for the different samples but generally included following processing steps: mechanical activation by grinding, pressing (50 kg/cm^2), annealing, and grinding. Here are presented the results of

the two samples where indium was at a doping level (marked as In_2O_3(3wt.%)/ZnO(97wt.%)-700°C/1h and In_2O_3(3wt.%)/ZnO(97wt.%)-950°C/1h) and one sample where the starting precursors had molar ratio around ZnO:In_2O_3=2:1 (marked as In_2O_3(54wt.%)/ZnO(46wt.%)-700°C/2h). The analytical standard of used PhACs, alprazolam ($C_{17}H_{13}ClN_4$) and amitriptyline hydrochloride ($C_{20}H_{24}ClN$) were purchased from Sigma-Aldrich. All chemicals were analytical grade. The NCPs loading was 1 mg/mL and the initial concentration of the investigated PhACs was 0.03 mmol/L. Before performing the photocatalytic experiment, samples were stirred in dark in order to achieve the adsorption-desorption equilibrium. Photocatalytic efficiency was measured after different time intervals. Samples were first filtrated through a Millipore (Millex-GV, 0.22 μm) membrane filter in order to remove ZIO NCPs from the aqueous solution, and then the appropriate aliquots (0.5 mL) were transferred into the vials and analyzed by ultra fast liquid chromatography with UV/Vis diode array detector (UFLC-DAD, Shimadzu) set at 222 nm and 206 nm which are the wavelengths of the alprazolam and amitriptyline maximum absorption, respectively. Scanning electron microscope, SEM (JEOL JSM-6460LV) was used to investigate the microstructure of the obtained ZIO NCP samples.

Results and discussion

The first results of the efficiency of ZIO NCPs in photocatalytic degradation of PhACs under simulated solar irradiation showed promising results [5]. Here are presented the comparative results of the photocatalytic degradation efficiency of three different ZIO NCPs and standard TiO_2 Degussa P25 in the degradation of alprazolam and amitriptyline (Fig. 1 shows the removal efficiency depending on the irradiation time).

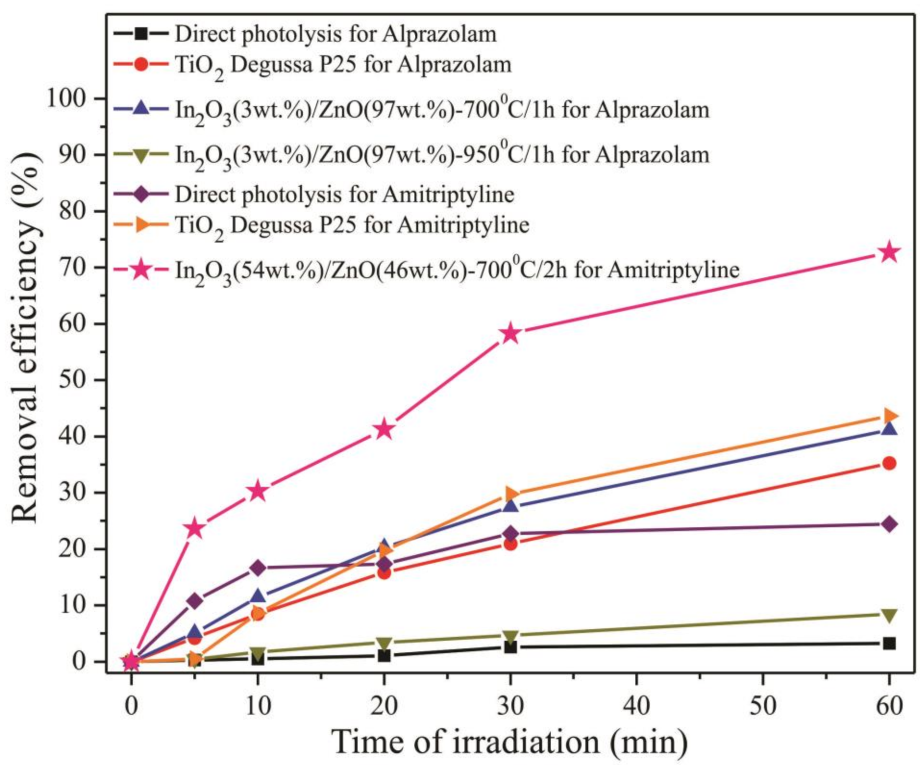

Figure 1. The removal efficiency of ZIO NCPs and TiO_2 Degussa P25 under SSI in the degradation of alprazolam and amitriptyline.

The ZIO NCP prepared at 950 °C showed no photocatalytic efficiency, while the sample marked as In_2O_3(3wt.%)/ZnO(97wt.%)-700°C/1h removed 41% of PhAC after the 60 min of SSI irradiation (Fig. 1). The most satisfactory removal of PhACs (73% of amitriptyline) was achieved in the presence of ZIO NCP which was prepared by grinding the starting precursor in the molar ratio of about 2:1, which were then annealed at 700 °C in air for two hours, and ground again, and was marked as In_2O_3(54wt.%)/ZnO(46wt.%)-700°C/2h (Fig. 1). Intensified indium incorporation at the higher annealing temperature (950 °C) should significantly reduce the particle size and shift the optical band gap towards the visible region when the starting indium concentration is at a doping level (samples with 3 wt.% of In_2O_3 and 97 wt.% of ZnO in Fig. 1). However, the occurrence of the unfavorable for the photocatalysis, the loss of the intrinsic defects such as oxygen vacancies and the formation of unstable In^{2+} ions, for the samples prepared at temperatures higher than 700 °C, could also accelerate the recombination rate and diminish the photocatalytic performance. The morphology and microstructure of the ZIO NCPs with significant photocatalytic efficiency, In_2O_3(3wt.%)/ZnO(97wt.%)-700°C/1h and In_2O_3(54wt.%)/ZnO(46wt.%)-700°C/2h were investigated by SEM and the example images are shown in Fig. 2.

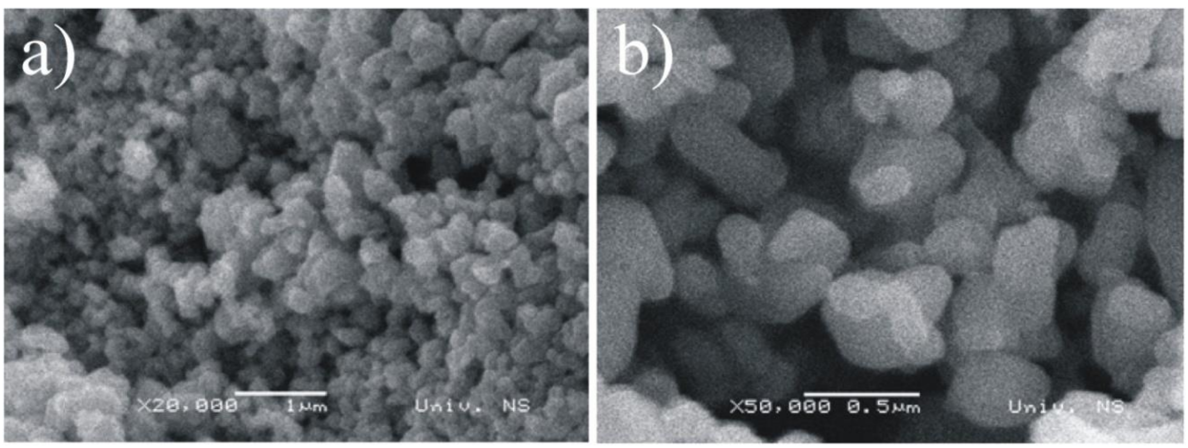

Figure 2. SEM images of ZIO NCPs, a) In_2O_3(3wt.%)/ZnO(97wt.%)-700°C/1h, and b) In_2O_3(54wt.%)/ZnO(46wt.%)-700°C/2h.

Conclusion

According to the obtained results, the ZIO NCP with ~46 wt.% of ZnO and ~54 wt.% of In_2O_3 is the most suitable for the photocatalytic degradation of the investigated PhACs. It's better photocatalytic performance compared to the other tested and differently prepared ZIO NCPs is believed to be a result of the synergetic effect of achieving better visible light activation through In_2O_3 absorption and charge separation mechanism obtained by ZnO and In_2O_3 band gap coupling, at the same time.

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