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Study of physicochemical and photocatalytic properties of ZnO nanopowders obtained by pulsed laser ablation

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Today, zinc oxide nanoparticles (NPs) have emerged as an efficient and promising material in different fields because of its unique properties [1]. The heterogeneous photocatalysis is attractive technology for the accumulation and conversion of solar energy for a wide range of environmental applications, such as disinfection, decolorization and purification of air and water. Along with the most studied titanium dioxide TiO2 in this field, ZnO is the closest alternative to it. Zinc oxide is a direct bandgap semiconductor with the band gap about 3.2-3.7 eV. The disadvantage of ZnO is that it absorbs light only in the UV region and only small fraction about 4-5% of the solar spectrum contains this range. Therefore, effective conversion of solar energy is still a problem. Various strategies have been employed to improve the photocatalytic efficiency of ZnO under visible light [2]. Doping by noble metals affects the rate of phase transfer of electrons and recombination of charge carriers due to the formation of new electronic traps, and also promotes the sensibilizatization of ZnO to the visible region of the spectrum. Pulsed laser ablation (PLA) has recently become a convenient, simple, effective and versatile approach to prepare different nanomaterials [3].

The aim of this work is to study the structure, morphology, optical and photocatalytic properties ZnO obtained by PLA of Zn metal target (99.99%) in water and air atmosphere, as well as powders modified with silver and gold (ZnO/Ag and ZnO/Au).

To obtain the initial ZnO powder a pulsed nanosecond Nd: YAG laser (1064 nm, up to 200 mJ, 7 ns, 20 Hz) was used. ZnO/Me (Me - Ag and Au, 10 mol.%) samples were prepared by impregnating ZnO nanopowders by aqueous AgNO3 and HAuCl4 solutions respectively and dried at 60 °C. Obtained initial ZnO and ZnO/Me samples were also annealed at 300 and 500 °C in a muffle furnace (with heating rate 10 °C/min) for 4 hours.

The phase composition of the powders was determined by X-ray diffraction patterns obtained with a Shimadzu XRD 6000 in the range of 2**0** = 10-70° with a scan rate of 2 °/min. The morphology and shape of ZnO NPs was investigated by transmission electron microscopy (TEM, Philips CM 12). Optical properties were examined using Cary 100 Varian spectrophotometer in the range from 200 to 800 nm. Photocatalytic activity of the powders was evaluated using 1.75×10^{-5} M aqueous solutions of organic dyes such as Rhodamine C and Methylene Blue upon light irradiation of Philips Master CDM-TD 70W/942 lamp (***k*** = 320-800 nm). Optical glasses WG305 (UV-visible) and GG410 (visible ***X*** > 410 nm) was used to investigate photocatalytic activity of obtained nanopowders depending on the irradiation light. The loss of the dye's concentration was evaluated by spectrophotometric measurements.

According to the XRD data initial ZnO nanopowder obtained PLA in air atmosphere has strong reflections of ZnO wurtzite phase, small amount of monoclinic Zn5(NO3)2(OH)2(H2O)2 and metallic Zn. ZnO obtained in water has no inclusion and consist only wurtzite phase. Modification ZnO lead to form Ag and Au NPs and strong XRD peaks were detected at higher annealing temperatures. UV-vis absorption spectra of ZnO and ZnO/Me samples clearly display an absorption in the UV region attributed to the band edge of ZnO and that in the visible region correspond to the localized surface plasmon absorption of Me nanoparticles respectively. As a result, modified nanopowders have better photocalalytic activity compared ZnO but annealing lead to decrease for dyes degradation possibly because of healing of defects and grain size growth.

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