Microwave assisted synthesis of nanocomposites in Zn-Sn-O-Ag system and their photocatalytic activity

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Abstract. The crystalline $\text{Zn}_2\text{SnO}_4$, $\text{Zn}_2\text{SnO}_4$/Ag and ZnO-$\text{Zn}_2\text{SnO}_4$ nanoparticles with specific surface area in the range of 24.1–28.5 m$^2$/g were prepared by combining microwave assisted synthesis with additional calcination at 900 °C. The parameters of the powders were compared with those of ZnO and ZnO/Ag nanoparticles prepared by microwave synthesis at 150 °C. The crystallite size of oxide and silver nanoparticles was in the range of 30–52 nm and 18–60 nm, respectively, depending on composition. The prepared nanoparticles showed high photocatalytic activity in degradation of methylene blue under ultraviolet and sunlight irradiation.

Key words: microwave synthesis, zinc oxide, stannate, silver, photocatalytic activity.

1. Introduction
Zinc oxide and zinc stannate are promising candidates for application in solar cells, sensors, medicine, cosmetic, photodegradation for degradation of organic pollutants due to their attractive electrical and optical parameters [1, 2]. The effective use of nanoparticles as photocatalysts depends on the particle size, morphology, crystallinity, and used dopants [3]. Besides this ZnO/$\text{Zn}_2\text{SnO}_4$ particulate composites show improved photocatalytic activity with respect to lone ZnO or $\text{Zn}_2\text{SnO}_4$ [4].

Due to the vast area of application of zinc oxide based nanoparticles, various their preparation methods, such as sol-gel, hydrothermal, combustion, precipitation, microwave synthesis have been elaborated [1, 2]. The hydrothermal synthesis is recognized well for preparation ZnO and $\text{Zn}_2\text{SnO}_4$ nanoparticles but particles size is relatively large [1, 5]. The promising fast and simple microwave synthesis ensures preparation of ZnO rod-like or quasi-spherical nanoparticles with size about 10–50 nm [6] or nanorods with length about 1.1 µm and diameter about 0.63 µm [7].

The aim of the present work was to extend microwave synthesis to preparation of nanoparticles in the Zn-Sn-O-Ag system with different content of the components and to compare their parameters and photocatalytic activity.

2. Experimental
Experiments were performed by using analytical grade chemicals. In the typical synthesis process separate solutions of 0.05 M of $\text{Zn(CH}_3\text{COO})_2\cdot\text{2H}_2\text{O}$ in 200 mL deionized water, 0.025 M of $\text{SnCl}_2\cdot\text{2H}_2\text{O}$ in 100 mL mixture of ethyl alcohol and methyl alcohol, and $\text{AgNO}_3$ in water (100 mL) were prepared. The appropriate amounts of the solutions were mixed and stirred. Water solution of formaldehyde for reducing silver was added. Afterwards NH$_4$OH or NH$_4$HCO$_3$ was added dropwise to reach pH 10. The mixture (500 mL) was stirred at room temperature and then transferred into a microwave reactor (Mastewave BTR (Anton Paar GmbH)) and treated at 120–160 °C and 9–11 bars for 5–30 min. The precipitates were separated by filtration and washed with deionized water. The obtained products were...
dried at 80 °C for 6 h. Afterwards Zn$_2$SnO$_4$ containing powders were calcinated at 850–900 °C in air in a furnace.

Phase and chemical composition of nanopowders was determined by X-ray diffraction (XRD) analysis (AdvanceD8, Bruker AXS), X-ray spectroscopy (S4Pioneer, Bruker AXS). The crystallite size was calculated from broadening of diffraction maxima using software Topas3 (Bruker AXS). Specific surface area (SSA) of powders was determined by the argon absorption-desorption method. Morphology and size of particles were determined by SEM.

Photocatalytic activity of the samples was evaluated by the degradation of methylene blue (MB) under direct ultraviolet (UV) irradiation of Hg lamp (120 W) at distance 110 mm and sunlight irradiation (18200 Lux, Luxmeter Lx-101B) in summer between 1 and 3 p.m. The aqueous solution of MB (7.6 × 10$^{-3}$ g/L) with catalyst (2g/L) was introduced in a quartz vessel and treated by ultrasound for 10 min in the dark to obtain homogeneous solution. During irradiation the solution was stirred mechanically and cooled by air flow.

The treatment of MB solution by UV and sunlight irradiation without catalyst showed that during 2 h the degradation degree MB reached 11 and 6% respectively. The samples of irradiated suspension were taken each 10 min for analysis. The degradation of MB was determined by measuring the light absorption by solution after removing solid particles at the wavelength of 622 nm using Jenway-6300 spectrometer.

3. Results and discussion

The XRD patterns of the as-prepared samples confirmed that microwave synthesis at 150 °C allows produce pure crystalline ZnO and ZnO/Ag but Zn$_2$SnO$_4$ powders contained admixture of ZnO and SnO$_2$. Pure crystalline Zn$_2$SnO$_4$ or Zn$_2$SnO$_4$/Ag nanoparticles were obtained after post-synthesis heat treatment at 850–900 °C for 2 h (Figure 1). After additional calcination up to 900 °C the crystallite size of Zn$_2$SnO$_4$ and Ag was the range of 32–52 nm and of 60 nm, respectively.

![X-ray diffraction patterns](image1)

**Figure 1.** X-ray diffraction patterns of the prepared nanoparticles: 1 – ZnO/Ag; 2 – Zn$_2$SnO$_4$; 3 – Zn$_2$SnO$_4$/Ag 2; o – Zn$_2$SnO$_4$; x – ZnO; + – Ag.

The parameters of samples prepared by microwave synthesis at 150 °C for 20 min and with additional calcination Zn$_2$SnO$_4$ containing samples at 900 °C for 2 hours are shown in Table 1.

The SSA of the prepared powders was in the range of 21.3–28.5 m$^2$/g and it was a little higher for Zn$_2$SnO$_4$ containing samples despite to high calcination temperature (Table 1). The determined
crystallite size of ZnO and Zn₂SnO₄ nanoparticles was in the range of 30–33 nm and 35–52 nm. The results provided evidence that presence of Ag had weak influence on crystallite size of ZnO.

Table 1. Parameters of the prepared nanoparticles

| Sample          | Ag content, mol% | SSA, m²/g | Crystallite size, nm |
|-----------------|------------------|-----------|----------------------|
| ZnO             | -                | 22.8      | 33                   |
| ZnO/Ag 1        | 1.0              | 22.9      | 32                   |
| ZnO/Ag 2        | 2.0              | 23.1      | 30                   |
| ZnO/Ag 3        | 3.0              | 21.3      | 31                   |
| Zn₂SnO₄         | -                | 24.1      | -                    |
| Zn₂SnO₄/Ag 2    | 2.0              | 25.9      | 35                   |
| Zn₂SnO₄/20ZnO*  | -                | 28.5      | 52                   |

* Zn₂SnO₄ sample contained 20 wt.% ZnO

The crystallite size of Ag nanoparticles was in the range of 18–60 nm depending on concentration of Ag. The determined typical particle size of ZnO in the range of 40–100 nm, especially particle size of Zn₂SnO₄ in the range of 30–80 nm, was close to the calculated crystallite size (Figure 2).

The morphology and particle size of the prepared ZnO powders differed strongly from nanotubes and nanosheets (0.5–2.0 µm) prepared by hydrothermal synthesis for 9–4 h at 90 °C [5] or from nanorods with a diameter 0.63 µm and length about 1.1 µm or flower-like ZnO particles prepared by microwave synthesis from zinc chloride solution [7]. The shape and size of the prepared stannate nanoparticles differed from cubic stannate nanoparticles with crystallite size about 500 nm [8] or from rod-like Zn₂SnO₄ nanoparticles with length about 300 nm and thickness of 50 nm prepared by hydrothermal synthesis [9]. Therefore applied synthesis ensures preparation of ZnO, ZnO/Ag and Zn₂SnO₄ as well as Zn₂SnO₄/Ag, Zn₂SnO₄-ZnO nanoparticles with relatively low crystallite and particle size.

Figure 2. SEM micrographs of ZnO (a); Zn₂SnO₄ (b); Zn₂SnO₄/Ag (c).

The crystallinity of prepared samples, their particle size, phase composition and presence of silver determined their photocatalytic activity under UV Hg lamp and sunlight. The photodegradation of MB under UV irradiation is shown in Figure 3. All tested powders showed good photocatalytic activity – they degraded MB up to 90–98% during 60–100 min depending on their composition. ZnO/Ag nanoparticles showed the highest photocatalytic activity. The low influence of silver on improvement of the catalytic activity of Zn₂SnO₄ can be connected with a large crystallite size of Ag particles. The photocatalytic activity of the prepared nanoparticles under UV irradiation of Hg lamp decreased in the following order: ZnO/Ag > ZnO > Zn₂SnO₄ > Zn₂SnO₄/20ZnO > Zn₂SnO₄/Ag > Zn₂SnO₄.
The important feature of the prepared nanopowders is their high photocatalytic activity under sunlight irradiation (Figure 4). The ZnO/Ag nanoparticles exhibited the highest photocatalytic activity again depending on content of silver. According to our studies the silver content of about 2% was optimal. The higher Ag content led to increase of the particle size causing decrease of the photocatalytic activity. The photocatalytic activity of the prepared nanoparticles under the sunlight irradiation decreased in the following order: ZnO/Ag > ZnO/Ag1 > Zn2SnO4/Ag2 > Zn2SnO4 > ZnO.

4. Conclusions
The combining microwave synthesis with additional calcination at 900 °C for 2 h ensures preparation of crystalline Zn2SnO4, ZnO-Zn2SnO4 and Zn2SnO4/Ag nanoparticles with specific surface area 24.1–28.5 m²/g close to that of ZnO and ZnO/Ag (21.3–22.8 m²/g) prepared by microwave synthesis at 150 °C for 20 min.

Crystalline size of ZnO and Zn2SnO4 nanoparticles was in the range of 30–33 nm and 35–52 nm, respectively, but crystalline size of Ag nanoparticles was in the range of 18–60 nm depending on the content of silver.

The prepared nanoparticles exhibited high photocatalytic activity in degradation of MB under UV and sunlight irradiation. ZnO and Zn2SnO4 doping with Ag enhanced their photocatalytic activity.
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5. References
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