ZnO–SnO₂–Sn nanocomposite as photocatalyst in ultraviolet and visible light

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Abstract
By combining ZnO with SnO₂, it is possible to obtain a photocatalyst with an extended lifetime and increased activity range in both ultraviolet and visible light. The paper presents the synthesis of ZnO–SnO₂–Sn nanocomposite. The morphology and structure of the samples were characterized by XRD, FTIR, SEM–EDS and TEM–EDX analysis. The results showed that the synthesised nanocomposites consisted of hexagonal ZnO, cubic SnO₂ and Sn nanoparticles. The results revealed that the highest removal efficiency (15.0%) of rhodamine B under visible light was achieved with ZnO–SnO₂–Sn consisting of 10% of SnO₂ and 5% of Sn, whereas the highest removal efficiency of methylene blue (95.6%) under UV light was achieved with ZnO–SnO₂–Sn consisting of 10% of SnO₂ and 1% of Sn. The presence of tin nanoparticles enhanced the photocatalytic properties directed towards visible light. The degradation of MB by ZnO–SnO₂–Sn remained above 80% even in the 5th cycle, while under visible light during photodegradation the RB removal efficiency decreased from 20 to 14%.

Keywords Tin oxide · Tin nanoparticles · Zinc oxide · Rhodamine B · Methylene blue · Photocatalysis

Introduction
Zinc oxide is a well-known inorganic nanomaterial and widely used due to its photocatalytic properties. Due to its photocatalytic, antimicrobial and optical properties, it can be used as an additive in industrial and consumer products (Mirzaei and Darroudi 2017; Chu et al. 2021). By adjusting the method to synthesize ZnO nanoparticles, it is possible to obtain rod-shaped, flower-shaped, cube-shaped, spherical nanoparticles, and such materials exhibit different properties (Singh and Dutta 2019). Zinc oxide, like titanium oxide, presents excellent photocatalytic properties (energy break ~ 3.37 eV, at room temperature and a large exciton binding energy of 60 meV). The material is characterized by low price, high availability and relatively high catalytic activity, however, compared to TiO₂, it tends to exhibit lower lifetime of photoactive states (Zdyb 2015).

The rapid recombination of photogenerated charge carriers reduces the efficiency of photocatalytic processes, hence it is advantageous to modify it by, among others, the addition of metal or metal oxide nanoparticles (Penke et al. 2020). Doping of ZnO with metal nanoparticles, e.g., Ag, Pt, Ni, Au or other semiconductors (ZrO₂, SnO₂, Bi₂O₃, NiO, CuO) inhibits electron–hole pairs recombination processes, extending the photocatalytic activity of ZnO (Pascariu et al. 2016).

Tin occurs on the +2 and +4 oxidation degrees to form tin(II) oxide and tin(IV) oxide, among others. Both oxides exhibit p-type semiconducting properties with a broad optical bandwidth of 2.5–4.3 eV (Barros et al. 2019). Priya et al. prepared tin(IV) oxide-modified zinc oxide nanoparticles with a size of 4 nm, reducing their energy band gap from 4.3 to 3.7 eV (Liu et al. 2018). Good visible light transmittance, chemical stability, conductivity and infrared reflectivity allow tin oxides to be used as additives for lithium batteries and solar cells, conductive surfaces and photocatalysts (Zhu et al. 2019; Zhao et al. 2021). Tin oxides, as an additive to titanium oxide, are used to obtain photosensitive solar cells which, using photon energy, enable the production of electricity (Mohanta and Ahmaruzzaman 2016). Ramasamy confirmed that coating the TiO₂ layer with tin oxide(IV) improved the open circuit voltage, leading to more than three times better power conversion efficiency. The high photovoltaic performance of the surface-modified mesoporous SnO₂
photoanode was mainly due to the inhibition of electron recombination caused by the passivation of reactive surface states and the increased dye charge (Sambasivam et al. 2019). Tin oxides show limited photocatalytic activity under visible light. Khalid et al. synthesised cube-shaped tin(IV) oxide nanoparticles with a size of 80–250 nm, which they successfully used as a photocatalyst in the degradation of Congo red under visible light (Khalid et al. 2018).

By combining ZnO with SnO₂, it is possible to obtain a photocatalyst with an extended lifetime and increased activity range in both ultraviolet and visible light. Literature successfully provides methods to obtain ZnO and SnO₂ based nanocomposites active under both UV and visible light (Lwin et al. 2019). Based on a two-step hydrothermal process combined with a microwave process, Xu et al. enabled the SnO₂ nanoparticles to grow uniformly into ZnO throughout the volume, reducing charge recombination along the heterojunction, thereby increasing the photocatalytic performance of the material (Xu et al. 2018). Chandra and Nath, increased the active surface area of the photocatalyst by depositing modified ZnO–SnO₂ on the surface of imidazolate zeolite. Through this process, they obtained a photocatalyst for methylene blue removal with a maximum photodegradation efficiency of 58.68% using 10 mg of material at a dye concentration of 1.6 mg/dm³ (Chandra and Nath 2020).

The limitation of ZnO–SnO₂ materials is the need for relatively long exposure time. A solution to this problem may be the use of tin nanoparticles, which would further increase the activity of the materials, reducing process time.

The aim of the research was to synthesize ZnO–SnO₂–Sn nanocomposites zinc sulphate (ZnSO₄·H₂O, Sigma Aldrich), sodium carbonate (Na₂CO₃, Sigma Aldrich), tin(IV) chloride (SnCl₄, Sigma Aldrich), tin(II) chloride (SnCl₂, Sigma Aldrich) and sodium borohydride (NaBH₄, Sigma Aldrich) were chosen.

Photocatalytic properties of the materials were verified in photodegradation of methylene blue (Sigma Aldrich) and rhodamine B (Sigma Aldrich) dyes. The influence of scavengers to determine the mechanism of photodegradation of dyes has been investigated with the application: triethanolamine (Sigma Aldrich), benzoquinone (Sigma Aldrich), mannitol (Sigma Aldrich) and silver nitrate(V) (Sigma Aldrich).

## Experimental

### Materials

As reagents to synthesis of ZnO–SnO₂–Sn nanocomposites zinc sulphate (ZnSO₄·H₂O, Sigma Aldrich), sodium carbonate (Na₂CO₃, Sigma Aldrich), tin(IV) chloride (SnCl₄, Sigma Aldrich), tin(II) chloride (SnCl₂, Sigma Aldrich) and sodium borohydride (NaBH₄, Sigma Aldrich) were chosen.

### Synthesis of ZnO–SnO₂–Sn: plan for mixtures with the restricted zone

The purpose of the research was to obtain material active in UV and visible light. Zinc oxide nanoparticles were modified with tin(IV) oxide which enhanced photocatalytic activity of the basic ZnO NPs and tin nanoparticles which enabled photodegradation of dyes in visible light. Firstly, ZnO NPs were synthesised using precipitation method. In the microwave reactor a dehydration process was carried out. Under ultrasonic irradiation 10 cm³ of 3 mol/dm³ ZnSO₄ solution was mixed with 20 cm³ of 1.7 mol/dm³ Na₂CO₃ solution. After 2 min, the suspension was transferred to a Teflon vessel to microwave reactor (Magnum II, Ertec) and it was heated via 15 min at 180 °C. The prepared ZnO NPs were washed several times and dried over 24 h in 105 °C. In the next step, solid ZnO NPs with known mass were added to solution of tin(IV) chloride. Under ultrasonic irradiation, a NaOH solution in stoichiometric quantity was dropped in. After 2 min, the suspension was transferred to a Teflon vessel into a microwave reactor (Magnum II, Ertec) and heated for 15 min at 180 °C. The prepared ZnO–SnO₂ NPs were washed several times and dried over 24 h at 105 °C. In the last stage, SnCl₂ solution was added to the solid ZnO–SnO₂ NPs. After 30 min of Sn²⁺ sorption process, NaBH₄ solution was dropped in. The reducing properties of NaBH₄ enabled to obtain tin nanoparticles adsorbed on ZnO–SnO₂ nanoparticles. The final material was rinsed thoroughly and dried at 70 °C for 24 h. The proposal mechanism of the reaction is presented as well:

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \xrightarrow{\text{microwave irradiation}} \text{ZnO} + \text{H}_2\text{O}
\]
The composition of the photocatalyst varied and was checked using a restricted mixture plan. The percentage concentration of the components is presented in the Table 1.

### Instrumental analysis

The structure of selected ZnO–SnO$_2$–Sn nanomaterials before and after the photocatalytic reaction was investigated by scanning electron microscopy (SEM) with EDS to obtain surface mapping, transmission electron microscopy (TEM) with Energy Dispersive X-Ray Analysis (EDX) and an elemental mapping using a Tecnai Transmission Electron Microscope, F20 X-Twin, FEI Europe. The Fourier Transform Infrared Spectroscopy (FTIR) method (Nicolet 380) was used to determining the effectiveness of sorption combined with its decomposition under the influence of UV and visible light. XRD analysis (Philips X’Pert camera with monochromator PW 1752/00 CuKα) determined the degree of crystallinity of materials and its phase composition.

### Optical studies

#### Photodegradation processes

The spectrum of degraded dyes and its concentration were examined by UV–Vis spectroscopy (Rayleigh UV-1800 spectrophotometer). The calibration curve was prepared at characteristics absorbance of each dye: 664 nm for MB and 554 nm for RB.

### Results and discussion

#### Selection of the final deposit based on the photocatalytic activity of the product in UV and Vis light

Table 2 presents the experimental results for the materials received. The sorption efficiency ($E_s$), photodegradation dye removal efficiency ($E_f$), total dye removal efficiency ($E_{total}$) and dye removal rate per gram of material ($R_D$) were calculated from the following equations:

$$R_D(mg/g) = \frac{(C_0 - C_t)V}{m}$$

$$E(\%) = \frac{(C_0 - C_t)}{C_0} \cdot 100,$$

where $C_0$ and $C_t$ are the initial and final concentrations of the dye solution (mg/dm$^3$) at time $t$, $V$ is the solution volume (dm$^3$), and $m$ is the mass of the material (g).

### Scavenging experiments for reactive species

The estimated contributions of selected ions and radicals to the photocatalytic degradation of MB and RB were determined. To a methylene blue solution (initial concentration 40 mg/dm$^3$) containing 100 mg ZnO–SnO$_2$(10)–Sn(1), 4 ml of scavenger solution was added and photodegradation was carried out under UV light. To the solution of rhodamine B (initial concentration 20 mg/dm$^3$) with 100 mg of ZnO–SnO$_2$(10)–Sn(5) 4 ml of the scavenger solution was added and photodegradation was carried out under Vis light. Triethanolamine [TEOA ($h^+$), $C_0 = 1$ mmol/dm$^3$], benzoquinone [BQ (·O$_2^-$), $C_0 = 0.5$ mmol/dm$^3$], mannitol [(·OH), $C_0 = 1$ mmol/dm$^3$] and silver nitrate(V) [AgNO$_3$ ($e^-$), $C_0 = 1$ mmol/dm$^3$] were used as scavengers. After 60 min, the solutions were filtered and the final dye concentrations were verified using a spectrophotometer (Sreedhar et al. 2019).
determined. Processes for pure ZnO were also carried out to compare the effect of SnO$_2$ and Sn addition on its properties. SnO$_2$ addition caused a slight decrease in the energy gap from 3.17 eV for pure ZnO to 3.15 eV for ZnO modified with 30% SnO$_2$ addition. The presence of tin compounds significantly improved the photodegradation efficiency of dyes in both visible and UV light. Before the right processes, photodegradation of MB and RB in different source of light was examined. Based on the study, the removal efficiencies under UV light of both MB and RB exceeded 50%, however, MB showed higher activity at higher concentration (50 mg/dm$^3$) hence this dye was selected for comparison of the activity of the materials. In the case of visible light process analysis, the activity of the photocatalyst decreased, which is consistent with the literature, due to the different energy delivered with UV light compared to visible light. Of the two dyes tested, RB showed higher activity hence this compound was chosen for comparative analysis of materials of varying composition (Table 3).

The highest dye removal efficiency in the ultraviolet photodegradation process was obtained for the material ZnO–SnO$_2$–Sn with SnO$_2$ 10% and Sn 1% content (Fig. 1a). The addition of Sn did not significantly improve photocatalytic properties, however, the presence of SnO$_2$ was significant (Fig. 1b). SnO$_2$ content at the level of 10% increases the share of ZnO. The higher the ZnO content, the higher the activity of the material, at the same time the presence of tin oxide(IV) is necessary to activate the ZnO surfaces and to prevent of the electro-hole pair recombination. The doping of Zn with SnO$_2$ results in electron deficiency in Zn which causes its tendency to act as an acceptor. On the surface of SnO$_2$, oxygen vacancies are formed, which act as a donor (Suthakaran et al. 2020). The highest dye removal efficiency in visible light photodegradation was obtained for ZnO–SnO$_2$–Sn with SnO$_2$ 10% and Sn 5% (Fig. 1c). In contrast to the processes under UV light, the addition of tin nanoparticles significantly improves the material properties in the presence of visible light (1D). An increase in nanoparticle content improved the dye photodegradation efficiency. Therefore, the materials with the highest efficiency for UV light, i.e., ZnO–SnO$_2$(10)–Sn(1) and for visible light, ZnO–SnO$_2$(10)–Sn(5), were used for further studies.

The effect of SnO$_2$ on enhancing the photocatalytic activity of ZnO was confirmed by Pascariu et al. Pure ZnO, pure SnO$_2$ and ZnO–SnO$_2$ mixtures were compared in the degradation processes of rhodamine B under visible light. The highest efficiency was obtained for the material with a Sn/Zn molar ratio of 0.03, i.e., about 6% of the addition of SnO$_2$ in the material, which is consistent with the results obtained in the study (Pascariu et al. 2016).

### Table 2

| Lp | mass ratio (–) | Band gap [eV] | MB photodegradation in UV light | RB photodegradation in Vis light |
|----|----------------|---------------|---------------------------------|---------------------------------|
|    | ZnO           | SnO$_2$       | Sn     | $E_s$ (%) | $E_f$ (%) | $E_{total}$ (%) | $R_D$ (mg/g) | $E_s$ (%) | $E_f$ (%) | $E_{total}$ (%) | $R_D$ (mg/g) |
| 1  | 0.89          | 0.10          | 0.01   | 3.16     | 1.5      | 94.1           | 95.6         | 10.91    | 7.1      | 0.6      | 7.7         | 0.62        |
| 2  | 0.69          | 0.30          | 0.01   | 3.15     | 4.9      | 56.0           | 60.8         | 2.61     | 6.2      | 0.3      | 6.5         | 0.53        |
| 3  | 0.85          | 0.10          | 0.05   | 3.16     | 0.8      | 86.9           | 87.7         | 9.07     | 10.6     | 4.4      | 15.0        | 1.2         |
| 4  | 0.65          | 0.30          | 0.05   | 3.15     | 6.9      | 58.4           | 65.2         | 3.74     | 6.8      | 3.8      | 10.6        | 0.85        |
| 5  | 0.87          | 0.10          | 0.03   | 3.16     | 2.1      | 89.4           | 91.6         | 10.06    | 4.3      | 2.5      | 6.8         | 0.55        |
| 6  | 0.67          | 0.30          | 0.03   | 3.16     | 7.2      | 64.7           | 71.9         | 5.19     | 5.2      | 2.2      | 7.4         | 0.58        |
| 7  | 0.79          | 0.20          | 0.01   | 3.15     | 2.7      | 76.3           | 79.0         | 6.99     | 5.2      | 2.9      | 8.1         | 0.63        |
| 8  | 0.75          | 0.20          | 0.05   | 3.17     | 7.9      | 63.4           | 71.3         | 5.08     | 8.7      | 4.1      | 12.8        | 1.05        |
| 9  | 0.77          | 0.20          | 0.03   | 3.16     | 1.7±0.3  | 75.8±6.4       | 77.4±4.4     | 6.69±0.29 | 6.3±0.6  | 2.4±0.3  | 8.7±0.3     | 0.69±0.15   |
| ZnO| 1 0 0         | 3.18          |        |          | 1.8      | 2.0           | 3.8          | 0.61     | 4.0      | 1.3      | 5.3         | 0.65        |

### Table 3

| Element | ZnO–SnO$_2$(10)–Sn(1) before photocatalysis | ZnO–SnO$_2$(10)–Sn(1) after photocatalysis | ZnO–SnO$_2$(10)–Sn(5) before photocatalysis | ZnO–SnO$_2$(10)–Sn(5) after photocatalysis |
|---------|--------------------------------------------|------------------------------------------|-------------------------------------------|-------------------------------------------|
| C (%)   | 2.72                                      | 3.14                                     | 2.82                                      | 2.79                                      |
| O (%)   | 27.00                                     | 22.49                                    | 26.48                                     | 31.58                                     |
| Zn (%)  | 60.53                                     | 64.36                                    | 53.35                                     | 55.65                                     |
| Sn (%)  | 9.75                                      | 10.01                                    | 15.35                                     | 9.98                                      |

Element ZnO–SnO$_2$(10)–Sn(1) and ZnO–SnO$_2$(10)–Sn(5) before and after photocatalytic processes.

Shanmugam and Jeyaperumal confirmed the favourable effect of Sn nanoparticles on the improvement of ZnO activity. Modification of ZnO with Sn and Cu nanoparticles decreased the energy gap of the material from 3.22 to 2.68 eV. The presence of tin and copper additives enabled photodegradation
processes under visible light, increasing the process rate by 2.6 times (Shanmugam and Jeyaperumal 2018).

**Characterization of the materials**

The shape and the composition of the materials $\text{ZnO–SnO}_2(10)–\text{Sn}(1)$ and $\text{ZnO–SnO}_2(10)–\text{Sn}(5)$ before and after photocatalysis processes were characterised using TEM–EDX and SEM–EDS analysis (Fig. 2). The both materials composed of zinc oxide triangular particles with small irregular particles of combination of $\text{ZnO}$ and $\text{SnO}_2$ nanoparticles (Fig. 2a, f). The average size of $\text{ZnO}$ was 522 and 475 nm for $\text{ZnO–SnO}_2(10)–\text{Sn}(1)$ and $\text{ZnO–SnO}_2(10)–\text{Sn}(5)$, respectively, while the $\text{ZnO–SnO}_2$ phase exhibited a particle size of 58.4 and 68.3 nm (Fig. 2c, d, h, i). On their surface, spherical tin nanoparticles were deposited with an average size of 16.1 and 15.0 nm for $\text{ZnO–SnO}_2(10)–\text{Sn}(1)$ and $\text{ZnO–SnO}_2(10)–\text{Sn}(5)$, respectively (Fig. 2e, j). The formation of 10–20 nm tin particles with a small proportion of 25–35 nm particles was observed.

The formation of crystalline $\text{ZnO}$ and polycrystalline $\text{ZnO–SnO}_2$ structure was confirmed from SAED patterns. From the measured ring diameters, the presence of planes (101) corresponding to $\text{ZnO–SnO}_2$ was confirmed, which is consistent with the XRD data. In the SAED image, the inter-plane spacing was measured to be approximately 0.250 nm, corresponding to (101) the plane of hexagonal $\text{ZnO}$ (Sharma et al. 2018). In $\text{ZnO–SnO}_2(10)–\text{Sn}(5)$, the presence of a plane (121) attributed to the Sn phase was also confirmed (Lee et al. 2018). The absence of reflexes corresponding to Sn in the $\text{ZnO–SnO}_2(10)–\text{Sn}(1)$ material was due to the low 1% metallic tin content in the product.

It was observed from SEM–EDS analysis that the tin content was higher in $\text{ZnO–SnO}_2(10)–\text{Sn}(5)$ compared to $\text{ZnO–SnO}_2(10)–\text{Sn}(1)$. After the photocatalysis process, tin nanoparticles were still present in the microphotographs (Fig. 3). The phenomena could be caused by an unequal occurrence of tin in the sample. No change in tin content was observed in the $\text{ZnO–SnO}_2(10)–\text{Sn}(1)$ sample. The high photocatalytic activity in successive cycles confirms the preservation of the material properties including the occurrence of tin nanoparticles.

The XRD analysis (Fig. 4a) confirmed the formation of $\text{ZnO–SnO}_2–\text{Sn}$, consisting of, cubic $\text{SnO}_2$ and Sn.
Fig. 2 TEM–EDX microphotographs of ZnO–SnO$_2$–Sn before photocatalytic process (a, k), ZnO–SnO$_2$–Sn before photocatalytic process (f, l), ZnO–SnO$_2$–Sn after photocatalytic process (m) and ZnO–SnO$_2$–Sn after photocatalytic process (n, c, h).

Fig. 3 SEM–EDS microphotographs of ZnO–SnO$_2$–Sn before photocatalytic process (a), ZnO–SnO$_2$–Sn before photocatalytic process (b), ZnO–SnO$_2$–Sn after photocatalytic process (e) and ZnO–SnO$_2$–Sn after photocatalytic process (d).
nanoparticles. The presence of additional crystalline phases has not been detected, which confirms the effectiveness of using microwave radiation to create a crystalline system of metal oxides. The presence of peaks at 2θ angles 31.79 (100), 34.40 (002), 36.27 (101), 47.57 (102) and 56.65 (110) correspond to hexagonal zincite ZnO (Shunmuga Sundaram et al. 2020). SnO2 embedded into the ZnO structure forming the ZnO–SnO2 phase (2θ = 17.69, 25.02, 29.08, 41.62, 55.0) (Salameh et al. 2017; Mohamed et al. 2021). In the material ZnO–SnO2(10)–Sn(5), the peaks corresponding to tin nanoparticles are characterized by a higher intensity compared to the material in which the tin mass content is 1% (2θ = 30.10 and 32.90) (Zeng et al. 2016). On the basis of FTIR tests (Fig. 4b) there were no changes in the structure of the photocatalyst after the dye degradation process. No characteristic groups corresponding to RB and MB dyes were observed. This indicates that no intermediates are deposited on the surface of the nanocomposite, which could limit the photodegradation efficiency.

**Kinetic studies on photocatalytic performance**

The kinetics of the degradation process of MB and RB dyes were determined for the materials with the highest photocatalytic efficiency under UV (ZnO–SnO2(10)–Sn(1)) and visible light (ZnO–SnO2(10)–Sn(5)). The pseudo-first-order Langmuir–Hinshelwood (L–H) kinetics model was used to determine the rate constant of the photodegradation reaction (Makama et al. 2020):

\[ \ln C = \ln C_0 - kt \]  

where \( k \) is the photodegradation rate constant (min\(^{-1}\))

![Figure 4 a XRD diffractograms and b FTIR spectrum of ZnO–SnO2(10)–Sn(1) and ZnO–SnO2(10)–Sn(5) before and after photocatalysis processes](image)

Figure 5a–d shows the degradation process of the dyes onto ZnO–SnO2(10)–Sn(1) at 90 min under UV light. High degradation efficiency was obtained for both methylene blue and rhodamine B. The rate constants were determined from the process results. For MB degradation, the rate constant was equal to 0.01018 min\(^{-1}\), and for rhodamine B the rate constant was 0.02673 min\(^{-1}\) (Table 4). For both processes, the degree of model fit showed high values, 0.9972 (for MB degradation) and 0.9802 (for RB degradation), confirming that the processes followed pseudo-first order kinetics (Fig. 5e, f). The processes carried out on ZnO–SnO2(10)–Sn(5) in the presence of visible light showed a limited degree of correlation. The process rate constants were 10 and 100 times lower, indicating a limited reaction rate. Combined with the low value of the determination coefficient, it can be concluded that the dye decomposition process under visible light followed a different mechanism than under UV light.

The results obtained in the study were compared with other materials used for photodegradation of dyes (Table 4). Pascariu et al. determined the effect of time, temperature and pH on the degradation of rhodamine B under UV light and visible light using ZnO–SnO2. By increasing the process temperature to 42 °C and pH to 9.5, the authors obtained an efficiency of 94.20% under visible light and 99.35% under UV light. Increasing the degradation time from 240 to 810 min allowed to increase the efficiency of photodegradation from 40% to over 94% (Pascariu et al. 2019) (Table 5).

**Cycle of the photodegradation processes**

The recyclability of the catalysts was verified through five cycles. The initial concentrations of methylene blue and
rhodamine B were 20 mg/dm³. After each process, the materials were filtered, washed and dried, and then reused in subsequent series of photodegradation process. Figure 6 shows a slight gradual decrease in the photodegradation efficiency of methylene blue under UV light and rhodamine B under visible light. The degradation of MB by ZnO–SnO₂(10)–Sn(1) remained above 80% even in the 5th cycle. During the photodegradation of RB under visible light, the removal efficiency decreased from 20 to 14%, which confirmed the good stability of the materials. The high reproducibility of ZnO and SnO₂-based materials was confirmed by Lin et al. ZnO–SnO₂ nanocomposites with an initial efficiency of 96.53% showed an activity 28.75% higher compared to pure ZnO, and after three cycles, the efficiency value of the material remained at 87.90% (Lin et al. 2018).

Effect of scavengers on dye degradation process

Hydroxyl radicals and superoxide anions and the presence of electrons and holes play an important role in dye degradation processes (Chu and Huang 2017). The presence of compounds such as benzoquinone, triethanolamine, isopropanol act as scavengers disrupting the equilibrium of photocatalytic reactions. The influence of radical and ion source compounds was investigated (Fig. 7). The presence of the selected scavenger allowed to study the effect of the selected radical or group on the decomposition process of MB and RB, allowing to predict the mechanism of this process.

To determine the mechanism of photocatalytic degradation, the role of different reactive oxidizing species was analyzed. Triethanolamine (TEOA (h⁺)), benzoquinone (BQ

| Table 4 | Langmuir–Hinshelwood kinetic parameters for photodegradation of methylene blue and rhodamine B solutions onto ZnO–SnO₂–Sn nanoparticles |
|---------|-----------------------------------------------------------------------------------------------------------|
|         | k (min⁻¹)  | C₀ (mg/dm³)  | C₀,ex (mg/dm³)  | R²      |
| ZnO–SnO₂(10)–Sn(1)–MB–UV | 10.18 × 10⁻³ | 50.17 | 51.45 | 0.9972 |
| ZnO–SnO₂(10)–Sn(1)–RB–UV | 26.73 × 10⁻³ | 16.35 | 16.39 | 0.9802 |
| ZnO–SnO₂(10)–Sn(5)–MB–Vis | 0.289 × 10⁻³ | 50.80 | 51.65 | 0.6132 |
| ZnO–SnO₂(10)–Sn(5)–RB–Vis | 2.761 × 10⁻³ | 14.50 | 15.20 | 0.9271 |

Fig. 5 Photodegradation of MB (C₀ = 40 mg/dm³) and RB (C₀ = 20 mg/dm³) solutions under different conditions: a degradation of RB in UV light on ZnO–SnO₂(10)–Sn(1), b degradation of MB in UV light on ZnO–SnO₂(10)–Sn(1), c degradation of RB in Vis light on ZnO–SnO₂(10)–Sn(5), d degradation of MB in Vis light on ZnO–SnO₂(10)–Sn(5) (catalyst mass = 200 mg, sample volume = 100 ml, t=60 min), e kinetics equations of photodegradation processes of RB in the UV and Vis light, f kinetics equations of photodegradation processes of MB in the UV and Vis light in the presence of ZnO–SnO₂–Sn nanoparticles.
(•O$_2^-$) and mannitol (OH) and silver nitrate(V) (AgNO$_3$ ($e^-$)) were used as scavengers. The ultraviolet degradation efficiency of the dye in the presence of compounds providing $h^+$, OH, $•O_2^-$ decreased by more than 50% compared to the system without additional compounds. The role of silver nitrate(V) in the process was not significantly affected by the use of electrons, in contrast to TEOA, which, using $h^+$ in the reaction, confirmed the crucial importance of holes. The presence of holes in catalytic processes carried out on ZnO was also confirmed by Verma et al. (2019). According to the authors, the holes can produce hydroxyl radicals from water or OH$^-$ and can react directly with dye molecules, leading to dye degradation. Therefore, removal of the holes by TEOA may result in inhibition of dye degradation. Reduction of the content of radicals $•$OH and $•O_2^-$ by introducing mannitol and benzoquinone had a negative effect on MB degradation. For processes under visible light, the addition of electron scavengers also caused a sharp decrease in photodegradation efficiency (Siva et al. 2020). A material with a tin content of 5% was used in the decomposition of rhodamine B. The significance of the presence of electrons on the decomposition process in visible light can be attributed to the presence of tin nanoparticles (Shanmugam et al. 2021). The metals present on the surface of the catalyst act as electron traps, reducing the recombination of electrons

### Table 5: Comparison of the photodegradation efficiency of methylene blue on pure ZnO and modified ZnO NPs

| Material                     | Dye                        | Light | $E$ (%) | References                  |
|------------------------------|-----------------------------|-------|---------|-----------------------------|
| ZnO                          | Methyl orange               | Visible | 76      | Shanmugam et al. (2021)    |
| Sn$^{4+}$-doped ZnO(2%)      |                             |       | 90      |                             |
| ZnO                          | Ethyl 4-hydroxybenzoate     | UV    | 50      | Sudrajat et al. (2021)     |
| ZnO                          | bisphenol A                 |       | 25      |                             |
| ZnO–SnO$_2 $(4%)             | Ethyl 4-hydroxybenzoate bisphenol A |       | 85      |                             |
| ZnO–SnO$_2 $(4%)             |                             |       | 90      |                             |
| SnO$_2$                      | methylene blue              | Visible | 37.0    | Guo et al. (2021)          |
| ZnFe$_2$O$_4$/SnO$_2$(10%)   |                             |       | 68.7    |                             |
| ZnO–SnO$_2$                  | Methyl orange               | UV    | 41.63   | Kumar et al. (2021)        |
| ZnO                          | Methylene blue              |       | 97.17   |                             |
| SnO$_2$                      | AR-183 dye                  | UV    | 38      | Dammala et al. (2019)      |
| ZnO–SnO$_2$                  |                             |       | 44      |                             |
| ZnO–SnO$_2$                  | rhodamine B                 | UV    | 99.35   | Pascariu et al. (2019)     |
| ZnO                          | tetracycline hydrochloride  | Visible | 45–50   | Lwin et al. (2019)         |
| SnO$_2$(50%)/ZnO             |                             |       | 90      |                             |
| ZnO                          | methylene blue              | UV    | 67.78   | Lin et al. (2018)          |
| ZnO–SnO$_2$                  |                             |       | 96.53   |                             |
| ZnO                          | Methylene blue              | UV    | 3.8     | This study                 |
| ZnO                          | Rhodamine B                 | Visible | 5.3    |                             |
| ZnO–SnO$_2$(10%–Sn(1%))      | Methylene blue              | UV    | 95.6    |                             |
| ZnO–SnO$_2$(10%–Sn(5%))      | Rhodamine B                 | Visible | 15.0   |                             |

![Fig. 6](image-url) Recycle efficiency of the photocatalysts: a ZnO–SnO$_2$(10%–Sn(1%)) during MB photodegradation in UV light, b ZnO–SnO$_2$(10%–Sn(5%)) during RB photodegradation in visible light.
and holes. The trapped electrons are transferred to oxygen to form superoxide radicals (Selvakumar et al. 2019).

**Mechanism of photocatalyst**

Based on the study of the effect of scavengers on the photodegradation process, a degradation mechanism was proposed as shown in Fig. 8. Due to the larger energy gap of SnO₂ (3.72 eV) compared to ZnO (3.35 eV), the CB photoinduced electrons in SnO₂ molecules can migrate to the CB of ZnO (Bakr 2016). The electrons generated in the conduction band of SnO₂ are used to react with molecules and O₂, which generates superoxide anions as a by-product. Simultaneously, photoinduced holes in the VB of SnO₂ nanoparticles can react with H₂O molecules via dissolved water, fragmenting them into hydroxyl (OH) groups (Chang and Wu 2019).

In the process of photodegradation by electromagnetic radiation having an energy greater than or equal to the prohibited break, the electron (e⁻) in the valence band (VB) can be excited to the conductivity band (CB) with a hole (h⁺) in VB. The photoelectron is trapped by electronic acceptors, i.e., O₂⁻ generated by tin nanoparticles. At the same time, photoinduced holes can easily be trapped by electron donors such as OH⁻. The presence of SnO₂ reduces the distance between the valence bands in the conduction, which will reduce the recombination of photogenerated electrons and holes.

\[
\text{MB} + h\nu \rightarrow \text{MB}^* \\
\text{ZnO} + h\nu \rightarrow \text{ZnO}(h^+_{\text{VB}}) + \text{ZnO}(e^-_{\text{CB}}) \\
\text{MB}^* + \text{ZnO}(h^+_{\text{VB}}) \rightarrow \text{MB}^+ + \text{ZnO} \\
\text{Sn}^{4+} + e^- \rightarrow \text{Sn}^{3+} \\
\text{Sn}^{3+} + \text{O}_2 \rightarrow \cdot\text{O}_2^- + \text{Sn}^{4+} \\
\cdot\text{O}_2^- + \text{H}^+ \rightarrow \cdot\text{OOH} \\
\cdot\text{OOH} + \cdot\text{O}_2^- + \text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \cdot\text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \\
\text{H}_2\text{O} + h^+_{\text{VB}} \rightarrow \text{H}^+ + \cdot\text{OH}
\]

**Fig. 8** Schematic diagram for the possible photocatalytic mechanism of ZnO–SnO₂–Sn under UV and visible light.
·OH + MB· → decomposition products.

The addition of Sn was shown to significantly affect the photocatalytic properties of ZnO–SnO2 under visible light. In visible light (λ > 420 nm), in the first step, photons are absorbed by the RB molecule, which enables the transfer of the photogenerated electron to the excited state via an intramolecular transition π–π∗: $RB + hv \rightarrow RB^·$.

In the presence of ZnO, the photoelectrons move to the conduction band of the semiconductor and the RB is converted to a cationic radical: $RhB^· + ZnO \rightarrow RhB^+ + ZnO(e^−_{CB})$.

The tin nanoparticles present on the surface limit the reduction of O2 by the electrons of CB ZnO: $ZnO(e^−_{CB}) + O_2 \rightarrow ·O_2^−$.

Between the bonding between SnO2 and Sn, reactions can occur to form tin cations. The close interaction of SnO2 doped Sn nanoparticles enables the oxidation of Sn by transferring electrons from the tin nanoparticles to the conduction band of SnO2:

SnO2 + Sn → SnO2(e−CB) + Sn2+  
Sn2+ + RB· → RB·+ + Sn  
SnO2(e−CB) + O2 → ·O2−.

The photodegradation efficiency of ZnO–SnO2–Sn is higher in the UV range than in the visible range. The absorption of incoming photons is much higher in the UV range than in the visible range, so if the samples are exposed to photons in visible light, the photosensitization of RB is less effective and the photodegradation efficiency is much lower (Ben Ali et al. 2016). The presence of tin nanoparticles affects the trapping of electrons on the catalyst surface and transferring them to open with oxygen peroxyl radical.

Conclusion

Sn-doped ZnO–SnO2 photocatalyst with a ZnO:SnO2:Sn mass ratio of 85:10:5 were successfully used as photocatalyst for photodegradation of rhodamine B under visible light, while ZnO–SnO2–Sn NPs with a ZnO:SnO2:Sn mass ratio of 85:10:1 were successfully used as photocatalyst for photodegradation of methylene blue under UV light. The microscopic studies indicate that the addition of tin nanoparticles has a dominant effect on the optical and structural properties of the nanocomposite. The presence of tin nanoparticles enhances the photocatalytic properties directed towards visible light. The degradation of MB by ZnO–SnO2–Sn remained above 80% even in the 5th cycle, while under visible light during photodegradation the MB removal efficiency decreased from 20 to 14%. Based on the study of the effect of scavengers on dye degradation, a mechanism for photocatalysis under both visible and UV light was proposed. The presence of tin nanoparticles affects the trapping of electrons on the catalyst surface and transferring them to open with oxygen peroxyl radical.

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Declaration

Conflict of interest  The authors report no declarations of interest.

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References

Bakr NA (2016) Effect of fluorine doping on structural and optical properties of SnO2 thin films prepared by chemical spray pyrolysis method. Adv Mater 5:23. https://doi.org/10.11648/j.am.20160504.12
Barros R, Saji K, Waerenborgh J et al (2019) Role of structure and composition on the performances of P-type tin oxide thin-film transistors processed at low-temperatures. Nanomaterials 9:320. https://doi.org/10.3390/nano9030320
Ben Ali M, Barka-Bouaifel F, Sieber B et al (2016) Preparation and characterization of Ni-doped ZnO–SnO2 nanocomposites: application in photocatalysis. Superlattices Microstruct 91:225–237. https://doi.org/10.1016/j.spmi.2016.01.014
Chandra R, Nath M (2020) Facile synthesis of ZnO–SnO2 anchored ZIF–8 nanocomposite: a potential photocatalyst. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-020-08936-5
Verma S, Tirumala Rao B, Jayabalan J et al (2019) Studies on growth of Au cube-ZnO core-shell nanoparticles for photocatalytic degradation of methylene blue and methyl orange dyes in aqueous media and in presence of different scavengers. J Environ Chem Eng 7:103209. https://doi.org/10.1016/j.jece.2019.103209

Xu M, Jia S, Chen C et al (2018) Microwave-assistant hydrothermal synthesis of SnO$_2$@ZnO hierarchical nanostructures enhanced photocatalytic performance under visible light irradiation. Mater Res Bull 106:74–80. https://doi.org/10.1016/j.materresbull.2018.05.033

Zdyb A (2015) Wybrane możliwości zastosowania nanostruktur w inżynierii środowiska. J Civ Eng Environ Archit 22:611–617. https://doi.org/10.7862/rb.2015.90

Zeng J, Xuan Y, Duan H (2016) Tin-silica-silver composite nanoparticles for medium-to-high temperature volumetric absorption solar collectors. Sol Energy Mater Sol Cells 157:930–936. https://doi.org/10.1016/j.solmat.2016.08.012

Zhao S, Shen Y, Maboudian R et al (2021) Facile synthesis of ZnO–SnO$_2$ hetero-structured nanowires for high-performance NO$_2$ sensing application. Sens Actuators B Chem 333:129613. https://doi.org/10.1016/j.snb.2021.129613

Zhu S, Liu J, Sun J (2019) Growth of ultrathin SnO$_2$ on carbon nanotubes by atomic layer deposition and their application in lithium ion battery anodes. Appl Surf Sci 484:600–609. https://doi.org/10.1016/j.apsusc.2019.04.163

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