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

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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 nanocomposite active under UV and visible light. The addition of metal nanoparticles to the surface of photocatalysts is well known to enhance the activity of the ZnO, however, the use of tin nanoparticles instead of the commonly used silver, gold or platinum is a cost-effective and safer solution. Moreover, the use of a tin-containing system allows for a stable and non-toxic material that is also active under visible light, which will allow the material to be used to remove harmful compounds under real conditions. Sn–SnO₂ heterojunction is formed by deposition of metallic Sn on the crystalline oxygen lattice of the formed SnO₂, which increases the amount of adsorbed oxygen on the photocatalyst surface. The obtained catalysts show higher photocatalytic activity compared to ZnO–SnO₂ under both UV and visible light. The Sn nanoparticles and adsorbed oxygen as photoinduced electron absorbers and electron scavengers, respectively, hinder the recombination of photoexcited electron–hole pairs, sequentially enhancing the photocatalytic activity.

Experimental

Materials

As reagents to synthesis of ZnO–SnO₂–Sn nanocomposites zinc sulphate (ZnSO₄·H₂O, Sigma Aldrich), sodium carbonate (NaCO₃, 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).

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 for 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:

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–SnO₂–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 CuK α) 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.

Table 1 The experimental plan for mixtures for synthesis of ZnO–SnO₂–Sn nanocomposites

Lp	Name of the materials	ZnO (% mass)	SnO ₂ (% mass)	Sn (% mass)
1	ZnO–SnO ₂ (10)–Sn(1)	89	10	1
2	ZnO–SnO ₂ (30)–Sn(1)	69	30	1
3	ZnO–SnO ₂ (10)–Sn(5)	85	10	5
4	ZnO–SnO ₂ (30)–Sn(5)	65	30	5
5	ZnO–SnO ₂ (10)–Sn(3)	87	10	3
6	ZnO–SnO ₂ (30)–Sn(3)	67	30	3
7	ZnO–SnO ₂ (20)–Sn(1)	79	20	1
8	ZnO–SnO ₂ (20)–Sn(5)	75	20	5
9	ZnO–SnO ₂ (20)–Sn(3)	77	20	3

The photodegradation of MB and RB in the presence of the ZnO–SnO₂–Sn nanoparticles was studied using batch experiments. The photocatalytic activity of the photocatalyst was investigated by measuring the degradation of MB from aqueous solutions under UV light using a UV lamp (wavelength = 360 nm) and the degradation of RB from aqueous solutions under visible light using a xenon lamp (400 nm $\leq \lambda \leq$ 800 nm). To 50 ml of dye solution, 200 mg of material was added under magnetic stirring for a specified time. The amounts of degraded R_D dye (mg/g) (2) and the photocatalytic degradation efficiency of MB or RB (3) were calculated from the following equations:

$$R_D(\text{mg/g}) = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$E(\%) = \frac{(C_0 - C_t)}{C_0} \cdot 100, \quad (2)$$

where C_0 and C_t are the initial and final concentrations of the dye solution (mg/dm³) at time t , V is the solution volume (dm³), 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/dm³) containing 100 mg ZnO–SnO₂(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/dm³) with 100 mg of ZnO–SnO₂(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/dm³], benzoquinone [BQ ($\cdot\text{O}_2^-$), $C_0 = 0.5$ mmol/dm³], mannitol [$(\cdot\text{OH})$, $C_0 = 1$ mmol/dm³] and silver nitrate(V) [AgNO₃ (e^-), $C_0 = 1$ mmol/dm³] 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).

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_p), total dye removal efficiency (E_{total}) and dye removal rate per gram of material (R_D) were

Table 2 Photocatalytic effectiveness in UV and visible light for ZnO–SnO₂–Sn nanocomposites differing mass ratio of the components

Lp	mass ratio (–)			Band gap [eV]	MB photodegradation in UV light				RB photodegradation in Vis light			
	ZnO	SnO ₂	Sn		<i>E_s</i> (%)	<i>E_f</i> (%)	<i>E_{total}</i> (%)	<i>R_D</i> (mg/g)	<i>E_s</i> (%)	<i>E_f</i> (%)	<i>E_{total}</i> (%)	<i>R_D</i> (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

determined. Processes for pure ZnO were also carried out to compare the effect of SnO₂ and Sn addition on its properties. SnO₂ 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% SnO₂ 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/dm³) 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–SnO₂–Sn with SnO₂ 10% and Sn 1% content (Fig. 1a). The addition of Sn did not significantly improve photocatalytic properties, however, the presence of SnO₂ was significant (Fig. 1b). SnO₂ 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 SnO₂ results in electron deficiency in Zn which causes its tendency to act as an acceptor. On the surface of SnO₂, 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–SnO₂–Sn with SnO₂ 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–SnO₂(10)–Sn(1) and for visible light, ZnO–SnO₂(10)–Sn(5), were used for further studies.

The effect of SnO₂ on enhancing the photocatalytic activity of ZnO was confirmed by Pascariu et al. Pure ZnO, pure SnO₂ and ZnO–SnO₂ 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 SnO₂ in the material, which is consistent with the results obtained in the study (Pascariu et al. 2016). 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

Table 3 Percentage content of the elements constituting ZnO–SnO₂(10)–Sn(1) and ZnO–SnO₂(10)–Sn(5) before and after photocatalytic processes

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

Fig. 1 Effect of mass ratio of SnO₂ and Sn nanoparticles on photocatalytic properties onto ZnO–SnO₂–Sn: **a** degradation of methylene blue in UV light, **b** optimization plot for the removal of MB by ZnO–

SnO₂–Sn with variable composition, **c** degradation of rhodamine B in visible light, **d** optimization plot for the removal of RB by ZnO–SnO₂–Sn with variable composition

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 ZnO–SnO₂(10)–Sn(1) and ZnO–SnO₂(10)–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 ZnO and SnO₂ nanoparticles (Fig. 2a, f). The average size of ZnO was 522 and 475 nm for ZnO–SnO₂(10)–Sn(1) and ZnO–SnO₂(10)–Sn(5), respectively, while the ZnO–SnO₂ 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 ZnO–SnO₂(10)–Sn(1) and ZnO–SnO₂(10)–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 ZnO and polycrystalline ZnO–SnO₂ structure was confirmed from SAED patterns.

From the measured ring diameters, the presence of planes (101) corresponding to ZnO–SnO₂ 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 ZnO (Sharma et al. 2018). In ZnO–SnO₂(10)–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 ZnO–SnO₂(10)–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 ZnO–SnO₂(10)–Sn(5) compared to ZnO–SnO₂(10)–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 ZnO–SnO₂(10)–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 ZnO–SnO₂–Sn, consisting of, cubic SnO₂ and Sn

Fig. 2 TEM-EDX microphotographs of ZnO-SnO₂(10)-Sn(1) before photocatalytic process (a, k), ZnO-SnO₂(10)-Sn(5) before photocatalytic process (f, l), ZnO-SnO₂(10)-Sn(1) after photocatalytic process (m) and ZnO-SnO₂(10)-Sn(5) after photocatalytic process (n), c, h

ZnO particle size distribution of ZnO-SnO₂-Sn, d, i ZnO-SnO₂ particle size distribution of ZnO-SnO₂-Sn, e, j Sn particle size distribution of ZnO-SnO₂-Sn, b SADE-TEM analysis of ZnO-SnO₂(10)-Sn(1), g SADE-TEM analysis of ZnO-SnO₂(10)-Sn(5)

Fig. 3 SEM-EDS microphotographs of ZnO-SnO₂(10)-Sn(1) before photocatalytic process (a), ZnO-SnO₂(10)-Sn(5) before photocatalytic process (b), ZnO-SnO₂(10)-Sn(1) after photocatalytic process (c) and ZnO-SnO₂(10)-Sn(5) after photocatalytic process (d)

Fig. 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

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 ($2\theta = 17.69, 25.02, 29.08, 41.62, 55.0$) (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% ($2\theta = 30.10$ 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):

$$\ln C = \ln C_0 - kt \quad (3)$$

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

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

Fig. 5 Photodegradation of MB ($C_0=40$ mg/dm³) and RB ($C_0=20$ 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

Table 4 Langmuir–Hinshelwood kinetic parameters for photodegradation of methylene blue and rhodamine B solutions onto ZnO–SnO₂–Sn nanoparticles

	k (min ^{−1})	C_0 (mg/dm ³)	$C_{0,ex}$ (mg/dm ³)	R^2
ZnO–SnO ₂ (10)–Sn(1)–MB–UV	10.18×10^{-3}	50.17	51.45	0.9972
ZnO–SnO ₂ (10)–Sn(1)–RB–UV	26.73×10^{-3}	16.35	16.39	0.9802
ZnO–SnO ₂ (10)–Sn(5)–MB–Vis	0.289×10^{-3}	50.80	51.65	0.6132
ZnO–SnO ₂ (10)–Sn(5)–RB–Vis	2.761×10^{-3}	14.50	15.20	0.9271

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

Material	Dye	Light	<i>E</i> (%)	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		41.63	Kumar et al. (2021)
	Methylene blue		97.17	
ZnO	AR-183 dye	UV	38	Dammala et al. (2019)
SnO ₂			44	
ZnO–SnO ₂			91	
ZnO–SnO ₂	rhodamine B	UV	99.35	Pascariu et al. (2019)
		Visible	94.20	
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 Recycle efficiency of the photocatalysts: **a** ZnO–SnO₂(10%)–Sn(1%) during MB photodegradation in UV light, **b** ZnO–SnO₂(10%)–Sn(5%) during RB photodegradation in visible light

($\bullet\text{O}_2^-$) 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^+ , $\bullet\text{OH}$, $\bullet\text{O}_2^-$ 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 $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ 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

Fig. 7 Photodegradation of MB and RB solutions under different scavengers (C_{AgNO_3} = 1 mMol, C_{TEOA} = 1 mMol, C_{mannit} = 1 mMol, C_{BQ} = 0.5 mMol, irradiation time 60 min)

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 ZnO 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).

Fig. 8 Schematic diagram for the possible photocatalytic mechanism of ZnO–SnO₂–Sn under UV and visible light

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.

Hydroxyl radicals are produced in the following process:

$\cdot\text{OH} + \text{MB}^* \rightarrow \text{decomposition products.}$

The addition of Sn was shown to significantly affect the photocatalytic properties of ZnO–SnO₂ under visible light. In visible light ($\lambda > 420$ 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 $\pi-\pi^*$:

In the presence of ZnO, the photoelectrons move to the conduction band of the semiconductor and the RB is converted to a cationic radical:

The tin nanoparticles present on the surface limit the reduction of O₂ by the electrons of CB ZnO:

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:

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 peroxy radicals. According to Verma et al., the addition of SnO₂ to ZnO increases the importance of superoxide anions, which affect dye degradation more than the presence of holes and hydroxyl radicals (Verma et al. 2018).

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 peroxy radical.

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Declaration

Conflict of interest The authors report no declarations of interest.

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