Microwave-synthesized ZrO2/ZnO heterostructures: fast and high charge separation solar catalysts for dyes-waste degradation

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Abstract
In 60 min, microwave-synthesized ZrO2/ZnO heterostructures exhibited high and fast sunlight photodegradation efficiencies for 50 ppm Congo red (CR) and 50 ppm methylene blue (MB) pollutants. ZrO2/ZnO heterostructures were characterized by XRD, SEM, EDX, FTIR, and diffuse reflectance (DR) techniques. The XRD analysis showed that these heterostructures have combined components of tetragonal ZrO2 and hexagonal ZnO phases. The SEM micrographs of all ZrO2/ZnO nanocomposites demonstrate the formation of nanospherical particles (major) and rod-like (minor) structures. The EDX spectra verified the presence of Zr, Zn and O elements with percentage ratios equivalent or close to that used during the experimental preparation. The FT-IR spectra showed the vibrational characteristic absorption modes of ZrO2 and ZnO bonds around 400–600 cm⁻¹. Two band gap energies were estimated corresponding to ZrO2 (5.05–5.16 eV) and ZnO (3.1–3.16 eV) components. Remarkably, in presence of ZrO2/ZnO (30/70 at%) heterostructure, the free solar energy initiated photodegradation efficiencies of 87% and 98% for 50 ppm CR and 50 ppm MB dyes after 60 min, respectively, which indicates the fast and superior photocatalytic activity of microwave-synthesized ZrO2/ZnO heterostructure. As well, this composition reveals good reusability and stability for three photocatalytic cycles. This uppermost photodegradation performance can be assigned to the high separation of charge carriers, especially for the ZrO2/ZnO (30/70 at%) nanocomposite.

Graphical abstract

Keywords Microwave-assisted hydrothermal · ZrO2/ZnO heterostructures · Wastewater · Organic dyes · Solar energy activated catalysis
1 Introduction

The elimination of dyes, herbicides, stimulants, pesticides and antibiotics as organic pollutants from the surrounding environment has become a serious world issue in the last years [1–3]. Water contaminated with residual dyes from the textile, printing press, paper, cosmetics, leather and other industries is the main source of many environmental problems [4–6]. Using solar energy-based semiconductor oxides in photocatalytic degradation of these types of organic pollutants seems to be a promising cost technique [7–9]. The light induces heterogeneous catalysis enables the conversion of organic pollutants such as dyes to molecules with higher biodegradability, finally leading to non-hazardous molecules (CO₂ and H₂O) [10, 11]. As a result, the search for advanced solar energy photo-reactive materials is of great importance environmentally and economically [12, 13]. In studies relating to the photocatalytic degradation of organic dye pollutants, zinc oxide (ZnO) nanostructures have been extensively candidates as a photocatalysts, owing to their high activity, long life span, low cost and its environmentally friendly nature [14–16]. However, the high recombination rate of the photogenerated charge carriers (electrons and holes pairs) acts as a limiting factor restricting the widespread applications of ZnO in photocatalysis [17, 18]. Recently, the ZnO based nanocomposites received a great attention of addressing these obstacles in an operative manner [19, 20]. To clarify, both of the metal oxides semiconductors were instantaneously excited and the electrons slip from the conduction band (CB) of one semiconductor to another while the holes moved to the valence band (VB) in the opposite direction [21–23]. These reactions have the ability to separate the electron–hole pairs which in turn enhanced the photocatalytic efficiency [21–23]. One of the metal oxide semiconductor materials that improve the photocatalytic properties of ZnO nanoparticles is zirconium oxide (ZrO₂) [24–26]. ZrO₂ belongs to a group of metal oxide semiconductor materials with relatively wide band gap energy over 5 eV [27]. In the past decade, the global research interest in wide band gap semiconductors has been significantly focused on ZrO₂/ZnO oxides due to their excellent properties as semiconductor materials [24–26]. The high electron mobility, high thermal conductivity, wide and direct band gap, good transparency, large exciton binding energy and easiness of synthesizing make ZrO₂/ZnO structure appropriate for a wide range of applications in optoelectronics, transparent electronics, lasing and sensing [28–30]. The replacement of Zn²⁺ by Zr⁴⁺ or versa vise can disturbs the charge balance in their lattices and the disturbed charge balance contributes to the adsorption of more hydroxide ions (–OH) on the surface of the particles of the powder, which additionally inhibits the recombination of the electron–hole pairs [21]. Congo red (CR) and methylene blue (MB) dyes have aromatic rings in their structures that are resistant to biodegradation and aerobic degradation. Therefore, it is essential to find operative methods that are useful for environmental protection and human health to remove these dyes from wastewater. In our previous study [21], we found that ZrO₂/ZnO (50:50) nanocomposite prepared by sol–gel method possesses degradation efficiencies of 99% and 97% for indigo Carmine (IC) (5 × 10⁻³ M) and MB (2.5 × 10⁻⁵ M) in 300 and 150 min, respectively. In this study, we made use of the major rewards of the microwave-activation hydrothermal technique to obtain nano-sized ZrO₂/ZnO heterostructures. These advantages include high purity synthesis circumstances, wide range of heating, perfect control of time, and the accessibility to achieve highly active powders with a narrow particle-size distribution. The effect of variation of Zr/Zn atomic ratio on the physicochemical and photocatalytic properties of the synthesized composites was evaluated. The synthesized ZrO₂/ZnO heterostructures were used as photocatalysts in the heterogeneous photodegradation of 50 ppm CR and 50 ppm MB dyes. Remarkably, the obtained results revealed that ZrO₂/ZnO heterostructure with composition of 30/70 at% has the highest ability to degrade the high concentrations of CR (50 ppm) and MB (50 ppm) in a short time of 60 min compared to ZrO₂/ZnO (50:50%) nanocomposite prepared by sol–gel method (300 and 150 min).

2 Experimental: synthesis, characterization and measurements

2.1 Materials and synthesis

Throughout the entire preparation part of this work, double distilled water, as well as the following reagent grade chemicals, were used: zinc acetate dihydrate Zn(CH₃COO)₂·2H₂O, zirconium hydroxide Zr(OH)₄, ethylene glycol and nitric acid (HNO₃) from Merck, Germany. ZrO₂/ZnO
nanocomposites were attained through the addition of calculated amounts of zirconium salt (dissolved in 10 ml of 4 N HNO3) to 50 ml aqueous solution of Zn(CH3COO)2·2H2O at the desired atomic percentage (at%) of ZrO2 = 10, 20, 30, and 40 at%. The mixture was stirred well, after that, 5 ml of ethylene glycol (complexing agent) was added drop by drop to stimulate the gelation process. The pH of the solutions was neutralized to 7 by slow addition of aqueous ammonia solution which speeds up the hydrolysis process and initiates the gelation process. After that, the mixture was poured into the Teflon vessel of the microwave reactor (MW) from Plazmatronika Ltd (Warsaw, Poland). The system runs at (600 W, 2.45 GHz, ERTEC microwave reactor). The duration of the reaction was 20 min, temperature 220 °C and power 100%. After the reaction was completed, the reaction vessel was cooled down for 20 min. The obtained powders were sedimented, separated from the solution by filtering and were washed with distilled water and isopropanol.

2.2 Characterization and photocatalytic properties measurements

The physical structure, lattice parameter and crystallite size of ZrO2/ZnO heterostructures with ZrO2 content of 10, 20, 30 and 40 at% were estimated by X-ray diffraction (XRD) with Cu Kα radiation of wavelength $\lambda = 1.5406$ Å (XRD, X’Pert PRO diffractometer, PANalytical BV, Almelo, Netherlands) and Rietveld refinement analysis. The morphological and elemental compositions of the synthesized ZrO2/ZnO heterostructures were investigated by the scanning electron microscope (Ultra Plus; Carl Zeiss Meditec AG, Jena, Germany) and energy-dispersive X-ray (EDX) technique. The vibrational absorption modes (Fourier transform infrared (FTIR) spectra) of ZrO2/ZnO heterostructures were detected through using a FTIR spectrometer (JASCO, model 4600). The absorption of wavelengths and the band gap energy were investigated using a double beam spectrophotometer-JASCO (model V-570 UV-Vis-NIR). At room temperature, the photodegradation rate of ZrO2/ZnO heterostructures was tested for CR and MB pollutants under direct free solar irradiation. In each experiment, the photocatalytic test was done by using CR solution with concentration of 50 ppm, MB solution of 50 ppm and 0.05 g of ZrO2/ZnO heterostructures. After mixing the ZrO2/ZnO heterostructure with CR (50 ppm, 100 ml) or MB (50 ppm, 100 ml), the mixtures were stirred for 20 min under dark condition. After this step, the mixed solution (ZrO2/ZnO heterostructure and dye) was placed under direct sunlight irradiation for 60 min. In total, 4 ml of the irradiated solution was withdrawn to measure the effect of time on dye decomposition. After removing the catalyst, the photocatalytic activity (%) was calculated by measuring the absorbance of the analytical samples using Schimadzu UV 3100, JP spectrophotometer.

3 Results and discussion

3.1 XRD study

Figure 1 depicts the XRD patterns of ZrO2/ZnO heterostructures with ZrO2 content of 10, 20, 30 and 40 at% prepared by hydrothermal method. The observed diffraction peaks of the microwave-synthesized ZrO2/ZnO powders were mainly indexed to wurtzite hexagonal structure of ZnO (JCPDS card No. 36-1451, space group P63mc) and tetragonal ZrO2 structure (JCPDS no. 79-1771, space group P42/nmc), signifying the formation of ZrO2/ZnO nanocomposites. In these patterns, the diffraction peaks located at nearly $2\theta = 31.86^\circ$, 34.48°, 36.31°, 47.64°, 56.93°, 62.94°, 66.45°, 68.01°, 69.15°, 72.73° and 77.02° were related to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) crystallographic planes of wurtzite hexagonal ZnO while the diffraction peaks situated at $2\theta = 30.85^\circ$, 50.08° and 60.02° were assigned to (111), (200) and (313) planes of tetragonal ZrO2. The intensities of the diffraction peaks of the tetragonal phase were increased with increasing the ZrO2 content from 10 to 40 at% (Fig. 1).

No observable diffraction peaks related to any secondary phases or any impurities were detected in the patterns. The crystallite sizes ($D$) of ZrO2/ZnO heterostructures were calculated based on Scherrer equation [30]:

$$D = \frac{0.89\lambda}{\beta\cos\theta},$$

where $\lambda$ is the X-ray wavelength, $\theta$ is the Bragg diffraction angle, 0.89 is Scherrer’s constant and $\beta$ is the full width at half maximum of the diffraction peaks. The calculated approximate values of the phase ratio, lattice parameters (a, b, c) and unit cell volume (V) of ZrO2 and ZnO components in ZrO2/ZnO heterostructures were determined by least-square Rietveld refinement based on FullProf software [31].

For all ZrO2/ZnO heterostructures, the profiles of the refinement data showed a well-fitting between the experimental and the calculated data, as represented in Fig. 2. Besides, no indication for any chemical products due to the reaction between ZrO2 and ZnO were detected and only the patterns confirmed the nanocomposites formation. As represented in Table 1, the measured phase ratio of ZrO2 is 8.5%, 18.8%, 31.2% and 36.8% for the nanocomposites with desired ZrO2 content of 10, 20, 30 and 40 at%, respectively, which in proximate values with that used in the preparation step. Based on the ionic radii database, the ionic radius of Zn2+ ion is 0.74 Å while that of Zr4+ is 0.72 Å with a clear difference only in the oxidation state. Consequently, it is anticipated that some of the Zr4+ ions can replace the Zn2+ ions into ZnO lattice or versa vise. Due to the difference in charge, Zn2+ cations can be acted as an acceptor dopant for Zr4+ sites and lead to oxygen vacancies formation while Zr4+ ions can act as donor dopants in ZnO.
lattice which injects more electrons. From the results in Table 1, there are some variations in the lattice parameter (a, b, c) and unit cell volume (V) of ZnO and ZrO2 due to the change in ZrO2 content in ZrO2/ZnO nanocomposites. The average crystallite size of the different ZrO2/ZnO heterostructures was calculated to be 45–51 nm, which confirms the formation of small nano-sized composites. Figure 3 illustrates the spacing-filling model and polyhedral crystal structure of hexagonal ZnO and tetragonal ZrO2.

3.2 SEM-EDX analysis: morphological and compositions

Figure 4 illustrates the scanning electron micrographs and the corresponding 3D view of ZrO2/ZnO heterostructures with ZrO2 content of 10, 20, 30 and 40 at% prepared by microwave-assisted hydrothermal method. The SEM micrograph of ZrO2/ZnO heterostructure with ZrO2 content of 10 at% shows the presence of two types of particles. The major type of these particles has a spherical shape while the minor type possesses an elongated shape, rod-like structure as shown inset Fig. 4a. When the content of ZrO2 reached 20 at%, more fine spherical nanoparticles are observed in addition to the rod-like structure. In the case of 30 at% ZrO2 similar architecture to that of 20 at% ZrO2 was formed. The micrograph of the ZrO2/ZnO heterostructure with ZrO2 content of 40 at% shows more uniform elongated particles in contact with very fine spherical nanoparticles. Focus shot on gathering of spherical nanoparticles (inset Fig. 4d) illustrates that the particles are homogenous and have a nearly similar size. The SEM micrographs of the synthesized ZrO2/ZnO heterostructures clearly show the enhancements in the size and homogeneity for the formed particles with increasing ZrO2 content. Elemental composition of ZrO2/ZnO heterostructures with Zr content from 10 to 40 at% were performed by EDX spectroscopy as shown in Fig. 5. Obviously, the characteristic peaks which corresponding to Zn, Zr and O elements were detected without any sign for the presence of any other impurities elements. With increasing the Zr content, the atomic percent (at%) of the Zn, Zr and O elements (inset Fig. 5) show gradual decreases for Zn element with steady increase for Zr.
The measured percentages of Zn, Zr and O elements in the different ZrO\textsubscript{2}/ZnO heterostructures are close to the experimental values and it is accepted within the normal error of the EDX technique.

### 3.3 FT-IR spectra

Figure 6 demonstrates the FTIR spectra of ZrO\textsubscript{2}/ZnO heterostructures with ZrO\textsubscript{2} content of 10, 20, 30 and 40 at\% synthesized by microwave-assisted hydrothermal route. Herein, the patterns show two vibrational absorption bands situated around 3428–3432 cm\textsuperscript{-1} and 1624–1627 cm\textsuperscript{-1} and both can be ascribed to the stretching and bending vibrational modes of the adsorbed H-O-H molecules on the surface of the ZrO\textsubscript{2}/ZnO heterostructures, respectively. The characteristic FT-IR vibrational absorption bands in the region of 525–409 cm\textsuperscript{-1} are attributed to the vibration modes of Zr-O and Zn-O bonds which confirm the formation of ZrO\textsubscript{2}/ZnO heterostructures. It can be seen that the intensities of these characteristic absorption bands were reduced with increasing the ZrO\textsubscript{2} content in the ZrO\textsubscript{2}/ZnO heterostructures. Besides, the shape of the bands become broader and extends over wide wavenumbers (cm\textsuperscript{-1}). The gradual effect of ZrO\textsubscript{2} on the IR properties is in agreement with the increase of ZrO\textsubscript{2} content noticed by the XRD analysis.

### 3.4 Optical properties

Table 1 Phases, lattice parameters (a, c), lattice parameters ratio (c/a), unit cell volume (V) and band gap of ZrO\textsubscript{2}/ZnO heterostructures

| Sample | Phases | a    | b    | c    | V     | Band gap (eV) |
|--------|--------|------|------|------|-------|---------------|
| 10%    | ZnO (91.5%) | 3.2508 | 3.2508 | 5.2082 | 47.6660 | 3.1           |
|        | ZrO\textsubscript{2}–T (8.5%) | – | – | – | – | 5.1 |
| 20%    | ZnO (18.8%) | 3.2508 | 3.2508 | 5.2081 | 47.6629 | 3.1           |
|        | ZrO\textsubscript{2}–T (81.2%) | 3.5962 | 3.5962 | 5.1523 | 66.6329 | 5.05          |
| 30%    | ZnO (68.8%) | 3.2505 | 3.2505 | 5.2081 | 47.6548 | 3.15          |
|        | ZrO\textsubscript{2}–T (31.2%) | 3.5976 | 3.5976 | 5.1755 | 66.9846 | 5.16          |
| 40%    | ZnO (63.2%) | 3.2511 | 3.2511 | 5.2092 | 47.6825 | 3.18          |
|        | ZrO\textsubscript{2}–T (36.8%) | 3.5952 | 3.5952 | 5.1420 | 66.4637 | 5.16          |

Figure 7 illustrates the ultraviolet–visible diffuse reflectance spectra of ZrO\textsubscript{2}/ZnO heterostructures with ZrO\textsubscript{2} content of 10, 20, 30 and 40 at\% synthesized by microwave-assisted hydrothermal route.
Fig. 3 Shows the a spacing-filling model crystal structure of hexagonal ZnO, b spacing-filling model crystal structure of tetragonal ZrO₂, c polyhedral crystal structure of hexagonal ZnO and d polyhedral crystal structure of tetragonal ZrO₂

hydrothermal technique. For all ZrO₂/ZnO heterostructures, the reflectance spectra exhibit two absorption lines (sharp decreases in intensity) below 400 and 250 nm which correlated to the band gap energies of ZnO and ZrO₂, respectively. It can be observed that the length of the absorption line (sharp decreasing in intensity) of ZnO was reduced with increasing ZrO₂ content while the length of the absorption line (intensity) of ZrO₂ was increased. The Kubelka–Munk equation, \( F(R) = (1 - R)^2/2R = \alpha/S \), was used to estimate the band gap energy of the two components in ZrO₂/ZnO heterostructures (i.e., ZrO₂ and ZnO) [32]. The relation between \( h\nu \) (eV, X-axis) and \( [F(R)h\nu]^2 \) (Y-axis) gives the band gap energy by lengthening the linear part of the curve to cut \([F(R)h\nu]^2 = 0\), as represented in Fig. 8 and tabulated in Table 1. The band gap energy of ZnO was found to be 3.1, 3.1, 3.15 and 3.18 eV, while the band gap energy of ZrO₂ was estimated to be 5.1, 5.05, 5.16 and 5.16 eV for ZrO₂/ZnO heterostructures with ZrO₂ content of 10, 20, 30 and 40 at%, respectively.

### 3.5 Photocatalytic properties under sunlight

Under free solar energy irradiation, the photodegradation efficiencies of ZrO₂/ZnO heterostructures with ZrO₂ content of 10, 20, 30 and 40 at% were assessed for decomposition of anionic CR (50 ppm, 100 ml) and cationic MB (50 ppm, 100 ml). Figures 9 and 10 demonstrate the variations of the maximum absorption peak of CR which located at 497 nm and that of MB situated at 668 nm in the presence of ZrO₂/ZnO (30/70 at%) heterostructure after exposed to sunlight irradiation of 60 min. For ZrO₂/ZnO (30/70 at%) heterostructure, obvious changes were detected in the maximum absorption peak of the CR (497 nm) and MB (668 nm) dyes after irradiation by sunlight with nearly complete vanishing of these peaks after 60 min. In case of ZrO₂/ZnO heterostructure with ZrO₂ content of 10, 20 and 40 at% (figures not included here) the decreasing in the maximum absorption peaks of both dyes is still good but less compared to ZrO₂/ZnO heterostructure of 30 at% ZrO₂ content. Figure 11 illustrates the whole photocatalytic efficiency of ZrO₂/ZnO heterostructures for CR (50 ppm) and MB (50 ppm) dyes after 60 min of sunlight radiation. For CR, the photodegradation efficiencies were estimated to be 52%, 70%, 87% and 74% for ZrO₂/ZnO heterostructures with ZrO₂ content of 10, 20, 30 and 40 at%, respectively. In case of MB, total efficiencies of 56%, 75%, 98% and 76% were detected for these catalysts,
Fig. 4 SEM and 3D images of ZrO₂/ZnO heterostructures with ZrO₂ content of a 10 at% ZrO₂, b 20 at% ZrO₂, c 30 at% ZrO₂ and d 40 at% ZrO₂ prepared by microwave-assisted hydrothermal method
respectively. Remarkably, these results confirm that ZrO2/ZnO heterostructure of 30 at% content possesses the highest efficiency for degradation of 50 ppm of both dyes in 60 min only. The observed enhancements in the photocatalytic activity of ZnO nanoparticles upon addition of 30 at% ZrO2 signifying that this composition...
possesses more efficient for separation of the photo-generated charge carriers (electron–hole pairs). The obtained results revealed that ZrO$_2$/ZnO (30/70 at%) heterostructure synthesized by microwave-assisted hydrothermal method has high activity and fast degradation time (60 min) for organic dyes in comparison with our previous study reporting degradation of MB and IC dyes using sol–gel-assisted ZrO$_2$/ZnO (50:50%) nano-composite in 300 and 150 min, respectively [21]. The mechanism for organic pollutant dyes degradation (CR and MB) in the presence of ZrO$_2$/ZnO heterostructure was linked to the excitation of electrons by the solar photon energy (Fig. 12). After placed the mixed solution under direct solar energy, the electrons in the VB of ZrO$_2$ and ZnO powders are transferred to their CB, generating electron–hole pairs. In solution, the excited electrons interact with the surround oxygen molecules (O$_2$) to create superoxide radicals (O$_2$•−) as reactive species along with hydrogen peroxide (H$_2$O$_2$). In a another process, the positive charge (holes) which formed in the VB react with water (H$_2$O) molecules and the hydroxyl species (–OH) to produce hydroxyl radicals (OH•) as reactive species. Between ZrO$_2$ and ZnO components, the electrons can transfer from the CB of ZrO$_2$ to the CB of ZnO while the holes (h$^+$) in the VB of ZnO can transfer to the VB of ZrO$_2$ which advance the electrons-hole pair’s separation. Efficiently, the hydroxyl radicals (OH•) and the superoxide radicals (O$_2$•−) hit the CR and MB
Fig. 12 Congo red (CR) and methylene blue (MB) degradation under solar energy irradiation in the presence of ZrO₂/ZnO heterostructures.

Fig. 13 Efficiency of ZrO₂/ZnO (30/70 at%) heterostructure toward methylene blue degradation for three cycles under solar irradiation.
molecules in the dirty solution and finally decompose them to non-toxic molecules (H₂O and CO₂). The total steps of the photocatalytic mechanism can be illuminated through the following chemical reaction [33–38]:

\[
\begin{align*}
\text{ZrO}_2/\text{ZnO} (30/70 \text{ at\%}) & \to \text{solar energy} \\
& \to \text{ZrO}_2(h^+ + e^-)/\text{ZnO} (h^+ + e^-) \text{ electron} - \text{hole pairs} \\
\text{ZrO}_2(h^+ + e^-)/\text{ZnO} (h^+ + e^-) & \to \text{ZrO}_2(h^+ + h^+)/\text{ZnO} (e^- + e^-) \\
\text{OH}^- + h^+ & \to \cdot \text{OH} \\
\text{H}_2\text{O} + h^+_{\text{VB}} & \to \cdot \text{OH} + \text{H}^+ \\
\text{O}_2 + e^- & \to \text{O}_2^- \\
2\text{H}_2\text{O} + 2\text{H}^+ + 3\text{O}_2^- & \to 3\text{H}_2\text{O}_2 + \text{O}_2 \\
\text{CR} \text{ and MB molecules} + \cdot \text{OH}/\text{O}_2^- & \to (\text{CO}_2 + \text{H}_2\text{O})
\end{align*}
\]

In this work, the obtained results show that the best composition for photocatalysis is ZrO₂/ZnO heterostructure with content of 30/70 at% and also revealed that the microwave-assisted hydrothermal technique is more effective for the photocatalytic applications of ZrO₂/ZnO heterostructure compared to sol–gel method used on our previous study on the same nanocomposite [21]. The microwave-assisted hydrothermal technique helps in reducing the photodegradation to 60 min compared to 150 and 300 min with maintaining the same efficiency and also perfect for high concentrations of organic pollutants [21]. The stability and reusability of ZrO₂/ZnO (30/70 at%) heterostructure (high efficient catalyst) was studied for the decomposition of MB dye at similar reaction circumstances. After the first photocatalytic experiment the catalyst was collected, washed with deionized water and dried at 90 °C for 1 h in air atmosphere to be used for the new degradation test. Figure 13 shows the results of MB degradation for three cycles. ZrO₂/ZnO (30/70 at%) photocatalyst reveals a good photo-stability for MB decomposition with efficiency of 98%, 92% and 85% for the first, second and third test under solar irradiation for 60 min, respectively. The obtained results point out that ZrO₂/ZnO (30/70 at%) photocatalyst is satisfactorily stable during the photo-decomposition of methylene dye.

4 Conclusion

ZrO₂/ZnO heterostructure (30/70 at%) exhibited a superior and fast sunlight photodegradation efficiency for high concentrations of CR (50 ppm) and MB (50 ppm) dyes. The XRD and Rietveld refinement results confirm the existence of two sets of diffraction peaks corresponding to tetragonal ZrO₂ and hexagonal ZnO structures. The morphological study of ZrO₂/ZnO heterostructures demonstrates the formation of a mixture of nanospherical particles (major) and rod-like (minor) structures in each composite. The EDX analysis shows the occurrence of Zr, Zn and O elements with a percentage ratio equivalent or closer to that used in the experimental preparation. Two band gap energies were estimated in each composite corresponding to ZrO₂ (5.05–5.16 eV) and ZnO (3.1–3.16 eV) components. The solar energy photodegradation efficiency of ZrO₂/ZnO (30/70 at%) heterostructure for 50 ppm CR and 50 ppm MB were found to be 87% and 98% after 60 min of solar energy irradiation, respectively, confirming the higher photocatalytic activity of ZrO₂/ZnO heterostructure. ZrO₂/ZnO (30/70 at%) heterostructure reveals good reusability and stability for three photocatalytic cycles. The significant photodegradation performance can be correlated to the high separation of charge carriers, especially for ZrO₂/ZnO (30/70 at%) heterostructure.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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