



Characterization and photoactivity of coupled ZnO–ZnWO₄ catalysts prepared by a sol–gel method

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ARTICLE INFO

Article history:

Received 7 December 2013

Received in revised form 18 February 2014

Accepted 22 February 2014

Available online 3 March 2014

Keywords:

Photocatalysis

ZnO–ZnWO₄ nanocomposites

Sol–gel method

Coupled semiconductors

ABSTRACT

ZnO–ZnWO₄ nanocomposites were synthesized by a novel sol–gel method and characterized through X-ray diffraction, BET specific surface area analysis, UV–Vis diffuse reflectance spectroscopy, scanning electron microscopy and transmission electron microscopy. The photocatalytic activity of the samples was evaluated using the degradation of 4-nitrophenol under UV light as probe reaction. The ZnO/ZnWO₄ molar ratio was varied in order to study its influence on the photoefficiency of the mixed samples. The ZnO–ZnWO₄ nanocomposites showed higher photoactivity than ZnO and ZnWO₄. The high efficiency of the mixed samples was explained by the coupling and the intimate contact of two different semiconductors having suitable energy levels of their conduction and valence bands that allow an improved charge separation of the photogenerated electron–hole pairs.

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1. Introduction

In the last two decades, heterogeneous photocatalysis has been the focus of a considerable attention in green chemistry, fine chemicals and in emerging “Advanced Oxidation Processes” (AOPs) [1–3] especially for air and water remediation [4].

When a photocatalyst is excited with photons of energy equal or higher than its band gap energy, electrons (e⁻) and holes (h⁺) pairs are created. In an aqueous or gaseous medium, reactants can react either with electrons or with holes. A good photocatalyst should adsorb reactants and absorb light efficiently preferably in the visible or near UV region of the electromagnetic spectrum.

Zinc oxide (ZnO) has been broadly studied as a photocatalyst due to its photosensitivity, and its attractive optoelectronic and catalytic properties. In many studies, ZnO was found efficient for the decomposition of many non-biodegradable organic compounds [5–9] due to the position of its valence band that gives a strong oxidizing power to the photogenerated holes. However, the photocatalytic activity of ZnO is limited by the recombination reaction of

the photogenerated electron/hole pairs that reduces the efficiency of the photocatalytic processes.

Coupling different semiconductors allows the vectorial displacement of electrons from one semiconductor to another, leading to a more efficient electron/hole separation and greater catalytic reactivity [10]. ZnO has been coupled to various semiconductors such as ZnO–TiO₂ [11–13], ZnO–CdS [14,15], ZnO–SnO₂ [16–21] to improve its photocatalytic activity. Only few publications have concerned the synthesis of ZnO–ZnWO₄ [22,23] and ZnO–ZnWO₄–WO₃ [24] photocatalysts to be employed for the photodegradation of organic compounds.

Zinc tungstate (ZnWO₄) is a promising material for applications in heterogeneous photocatalysis due to its interesting physical and chemical properties [25–39]. Zhu and coworkers reported that ZnWO₄ exhibited relatively high photocatalytic activity for the degradation of aqueous solutions of rhodamine B [25–31] and methylene blue [30,37] and also for gaseous formaldehyde [26–28]. ZnWO₄ was efficient for the decomposition of salicylic acid [35] and the decoloration of methyl orange [37], malachite green [36,38] and rhodamine 6G [33]. Up to now ZnWO₄ photocatalysts have been synthesized by a variety of different processes including co-precipitation [26], hydrothermal methods [28–33], microwave assisted techniques [35,39] and mechanochemical synthesis at room temperature [38].

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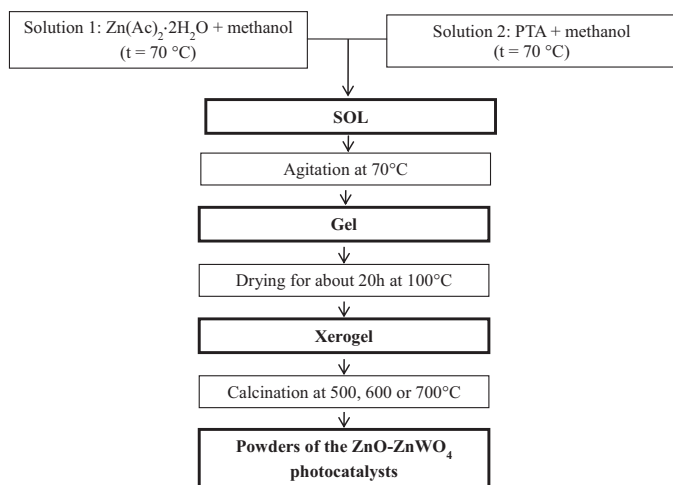


Fig. 1. Flowchart of the synthesis of the ZnO–ZnWO₄ photocatalysts.

In the present paper we report the synthesis of ZnWO₄ and ZnO–ZnWO₄ photocatalysts obtained by a novel sol–gel method. The photocatalytic activity of the samples was evaluated using the degradation of 4-nitrophenol (4-NP) chosen as a probe molecule because substituted phenols are ubiquitous contaminants in water streams [40]. The influence of the ZnO/ZnWO₄ molar ratio and the calcination temperature was investigated. Photovoltage measurements were also carried out to seek a correlation between the relative positions of the energy bands of ZnO and ZnWO₄ and the photocatalytic activity of the coupled catalysts.

2. Experimental

2.1. Synthesis

Zinc acetate dihydrate (Sigma–Aldrich), phosphotungstic acid hydrate (Sigma–Aldrich) and methanol were used as received without any further purification.

The ZnO–ZnWO₄ mixed photocatalysts were synthesized according to the flowchart presented in Fig. 1. Solution 1 and solution 2 were prepared by dissolving Zn(Ac)₂·2H₂O and H₃PW₁₂O₄₀·xH₂O (PTA) in methanol under stirring at 70 °C. Amounts of Zn(Ac)₂·2H₂O and PTA corresponding to an equal number of Zn and W atoms were used to prepare pure ZnWO₄. The amounts of precursors were opportunely determined in order to obtain powders with molar ratios ZnO/ZnWO₄ equal 1/0.02, 1/0.05, 1/0.25. The samples were labeled ZnO, Zn–ZW_{0.02}, Zn–ZW_{0.05}, Zn–ZW_{0.25}, and ZnWO₄. Solution 1 was added slowly to solution 2 and the mixture was aged for about 2 h to obtain the sol. The natural pH of the sol was always about 5 whatever the molar ratio. A gel was formed by stirring the sol for some hours at 70 °C. Then, the obtained gel was dried for about 20 h at 100 °C to produce the xerogel. Finally, the photocatalysts were obtained by calcining the xerogel for 2 h at different temperatures (500, 600 or 700 °C). Pure ZnO was synthesized by using only Zn(Ac)₂·2H₂O as the precursor.

2.2. Characterization

X-ray diffraction patterns of the powders were recorded at room temperature by an Ital Structures APD 2000 powder diffractometer using the Cu K α radiation and a 2 θ scan rate of 2°/min.

The mean grain size of the photocatalysts was estimated using the Debye–Scherrer equation:

$$D = 0.9\lambda / \beta \cos \theta \quad (1)$$

where D is the mean grain size (nm), λ is the wavelength of the X-ray radiation (0.154 nm), β is the corrected full width at half maximum height and θ is the diffraction angle. The specific surface area (SSA) of the samples was determined with a Micro-metrics Flow Sorb 2300 instrument by using the single-point BET method. UV–Vis diffuse reflectance spectra (DRS) of the samples were recorded by using a Shimadzu UV-2401PC spectrophotometer. BaSO₄ was used as a reference and the spectra were recorded in the range 200–800 nm.

The morphology of the catalysts was examined using a Philips XL30 ESEM scanning electron microscope (SEM), operating at 30 kV on specimens upon which a thin layer of gold was deposited. Transmission electron microscopy (TEM) measurements were obtained using a JEM-2100 (JEOL, Japan) operating at 200 kV accelerating voltage, equipped with an energy dispersive X-ray spectrometer (EDS, Oxford, UK) suitable for element identification. The powders were dispersed in isopropanol and a small drop was deposited on a 200 mesh carbon-coated copper grid, which was introduced into the TEM chamber analysis after complete solvent evaporation.

2.3. Photovoltage measurements

Photovoltage measurements were performed in a Pyrex reactor with a total volume of 150 mL. 100 mg of the photocatalyst were added to 100 mL of a 0.1 M NaNO₃ solution. A platinum electrode was used as working electrode and the reference was an Ag/AgCl electrode. After degassing for 30 min with N₂, 20 mg of methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dichloride) were added to the suspension. Then, the mixture was once more degassed for 30 min. The pH was adjusted using HNO₃ and NaOH solutions. During the experiments the suspension was irradiated by two UV lamps (Philips HPK 125 W). The values of pH and potential (V) were measured using a pH meter Thermo Orion 720A and a multimeter Metex 3800, respectively.

2.4. Photocatalytic experiments

A cylindrical Pyrex batch photoreactor containing 0.15 L of the 4-NP solution (20 mg/l) was used to perform the photodegradation experiments. For each photocatalytic run the amount of photocatalyst was chosen in order to ensure that almost all the photons emitted by the lamp were adsorbed by the suspension. The photon flux was measured using a radiometer (Delta Ohm DO9721 with a UVA probe). The light source was a 125 W medium pressure Hg lamp (Helios Italquartz, Italy) with a maximum emission at about 365 nm, axially positioned within the photoreactor. The temperature of the suspension was controlled by circulation of water through a Pyrex thimble surrounding the lamp. A magnetic stirrer was used to guarantee the homogeneity of the reacting mixture. Before the light was turned on, the suspension was kept in the dark for 2 h to reach the adsorption–desorption equilibrium. Samples were taken at different time intervals to evaluate the progress of the 4-NP degradation. Each sample was filtered by a 0.2 μ m filter and the residual 4-NP concentration was measured by the UV–Vis spectrophotometer.

After the photocatalytic run, the powders were sometimes recuperated, washed with distilled water and a fresh solution of 4-NP was added to test the reusability of the catalysts.

3. Results

3.1. Structural and morphological characterization

Fig. 2 shows the X-ray patterns of the photocatalysts calcined at 600 °C for 2 h. Pure ZnO, ZnWO₄ and mixed ZnO–ZnWO₄ samples were obtained with the present sol–gel protocol. The main

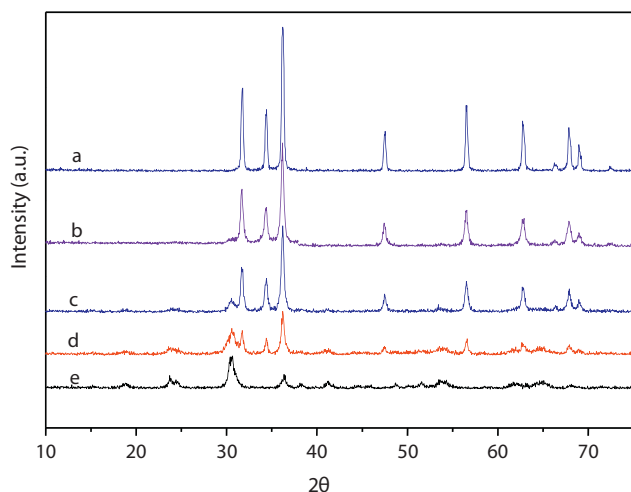


Fig. 2. XRD patterns of (a) ZnO, (b) Zn-ZW_{0.02}, (c) Zn-ZW_{0.05}, (d) Zn-ZW_{0.25} and (e) ZnWO₄ calcined at 600 °C for 2 h.

peaks were indexed corresponding to hexagonal ZnO (JCPDS card number: 36-1451) and monoclinic ZnWO₄ (JCPDS card number: 15-0774). The peaks of pure ZnWO₄ were broad and not well defined, due to a low crystallinity. The peaks related to ZnWO₄ were detected in Zn-ZW_{0.25} but were very small for Zn-ZW_{0.05} and just appreciable for Zn-ZW_{0.02}. No characteristic peaks of other compounds such as WO₃ were observed.

Fig. 3 shows representative X-ray patterns of Zn-ZW_{0.25} samples calcined for 2 h at 500, 600 or 700 °C. The peaks of both phases became sharper with increasing temperature indicating a growth of the size of the particles. These results are in good accordance with

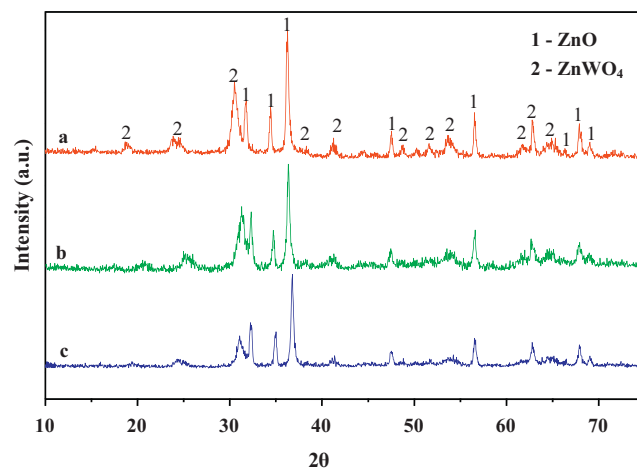


Fig. 3. XRD patterns of Zn-ZW_{0.25} calcined for 2 h at different temperatures: (a) 700 °C, (b) 600 °C and (c) 500 °C.

the measurements of specific surface area whose values decreased from 27.3 m²/g at 500 °C to 12.6 m²/g at 700 °C.

The average grain sizes of the various samples determined by using the diffraction peaks (1 0 1) for ZnO and (1 1 1) for ZnWO₄ are reported in Table 1. The crystal size of ZnO in the ZnO-ZnWO₄ samples was lower than that determined for pure ZnO indicating that the presence of ZnWO₄ inhibits the growth of the ZnO particles. As shown in Table 1 the specific surface areas of the mixed photocatalysts were higher than those of pure ZnO or ZnWO₄.

The surface morphology of the samples has been analyzed by SEM and HR-TEM images. Fig. 4 shows SEM micrographs of pure ZnO, pure ZnWO₄ and Zn-ZW_{0.05} calcined at 600 °C for 2 h. All the samples consisted of aggregates of particles whose average sizes

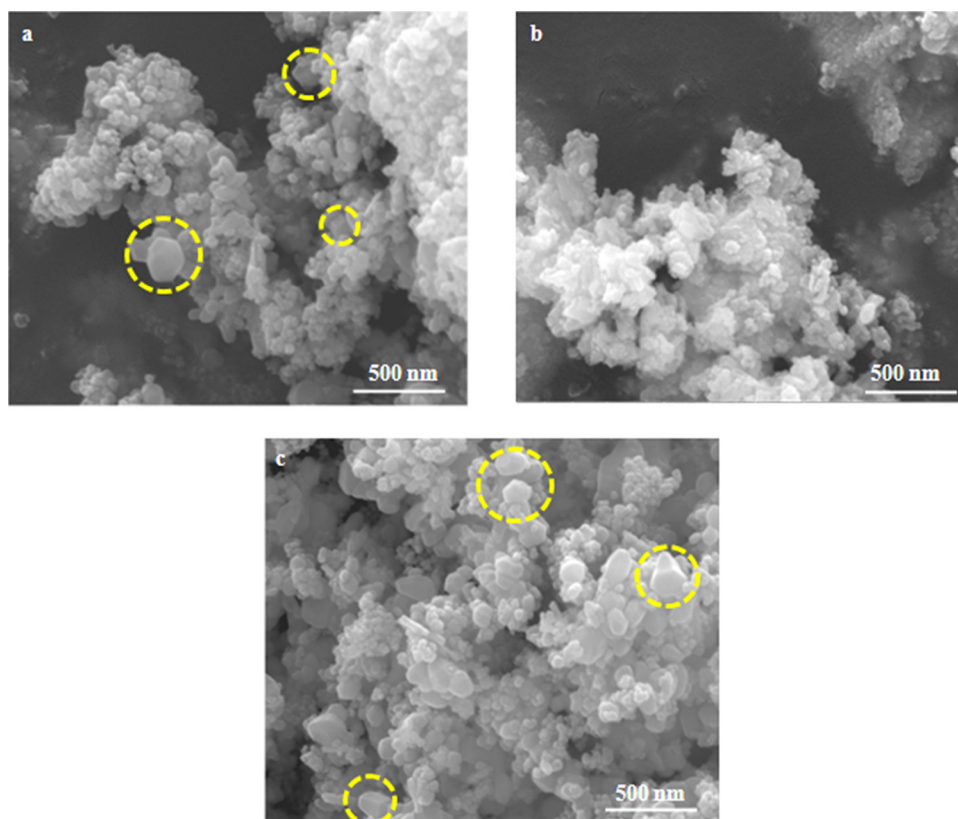


Fig. 4. SEM micrographs of (a) ZnO, (b) ZnWO₄ and (c) Zn-ZW_{0.05}.

Table 1
Physical characteristics of pure ZnO, pure ZnWO₄ and ZnO–ZnWO₄ nanocomposites.

	ZnO 600 °C/2 h	ZnWO ₄ 600 °C/2 h	ZnZW _{0.02} 600 °C/2 h	ZnZW _{0.05} 600 °C/2 h	ZnZW _{0.25} 500 °C/2 h	ZnZW _{0.25} 600 °C/2 h	ZnZW _{0.25} 700 °C/2 h
Mean size of ZnO (nm)	30.0	–	26.1	26.2	23.3	26.1	26.2
Mean size of ZnWO ₄ (nm)	–	12.0	–	12.1	9.1	11.4	12.1
SSA (m ² /g)	4.3	12.9	18.0	19.7	27.3	18.6	12.6
Band gap (eV)	3.20	3.14	3.21	3.22	3.23	3.23	3.22

appeared quite close to those calculated from the XRD patterns. As shown in Fig. 4a, the particles of pure ZnO had a hexagonal-like shape (a small number of hexagons are indicated by circles) whereas the particles of ZnWO₄ (Fig. 4b) were rather irregular. The micrographs of the mixed ZnO/ZnWO₄ samples revealed the presence of both morphologies. Fig. 4c shows the representative SEM image of ZnZW_{0.05}. As highlighted by circles, the small crystallites of the different phases were interwoven with each other forming tightly bound nanoclusters.

Fig. 5 shows HR-TEM images of ZnZW_{0.25} calcined at 600 °C for 2 h. The sample was composed of nanoparticles with sizes in the range of about 70–150 nm (Fig. 5a) and each nanoparticle was attached to several other nanoparticles. Fig. 5b reveals the

formation of a junction between two nanoparticles with different morphologies. As shown in Fig. 5c, the energy dispersive spectroscopy (EDS) analysis confirmed that the sample consisted of Zn and W elements (copper came from the grid of the sample holder) which is consistent with the XRD results.

3.2. DRS spectroscopy

Fig. 6 shows the UV–Vis absorption spectra of the various samples. All the photocatalysts were responsive in the ultraviolet region but pure ZnWO₄ exhibited a very low intensity probably due to its poor crystallinity.

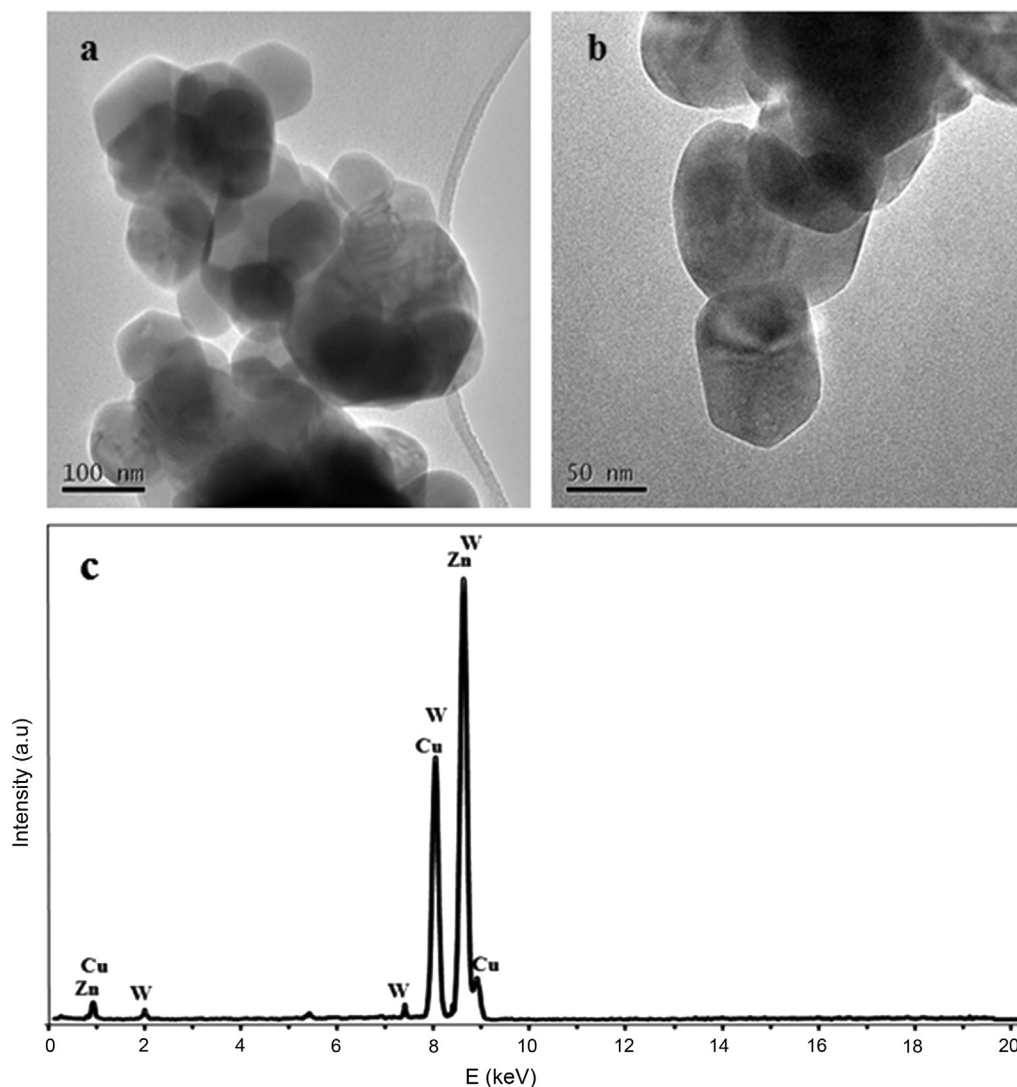


Fig. 5. (a, b) TEM images and (c) EDS spectrum of Zn–ZW_{0.25}.

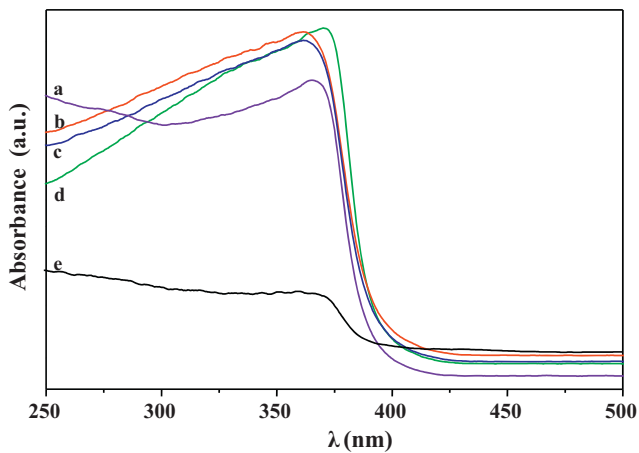


Fig. 6. UV-vis absorption spectra of (a) Zn-ZW_{0.25}, (b) Zn-ZW_{0.02}, (c) Zn-ZW_{0.05}, (d) ZnO and (e) ZnWO₄.

The band gap values (E_g) of the photocatalysts were estimated by extrapolation of the linear part of the plots of $(\alpha h\nu)^2$ versus the energy of the exciting light assuming that all the samples were direct crystalline semiconductors [41]. As shown in Table 1, the E_g values of ZnO and ZnWO₄ were 3.20 and 3.14 eV, respectively. The band gap values of the samples containing ZnO and ZnWO₄ ranged between 3.21 and 3.23 eV and were scarcely dependent on the ZnO–ZnWO₄ ratio.

3.3. Photovoltage measurements.

The values of the flat band potential (E_{FB}) of the ZnO and ZnWO₄ samples were determined by the slurry method proposed by Roy et al. [42], measuring the variation of the photovoltage with the pH of suspensions of the powders in the presence of an electron acceptor. Fig. 7 shows the photovoltage vs pH curves obtained by irradiation of ZnO and ZnWO₄ suspensions in the presence of methyl viologen dichloride. The pH value of the inflection point (pH_0) of the obtained sigmoidal curves allows calculating the flat band potential at pH 7 by the equation:

$$E_{FB}(pH = 7) = E_{MV^{2+}/MV^{+}}^0 + 0.059(pH_0 - 7). \quad (2)$$

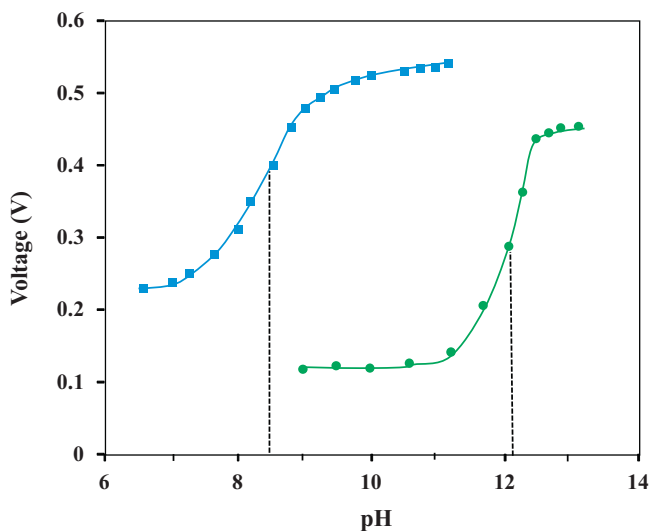


Fig. 7. Effect of pH on the photovoltage developed by irradiation of (■) pure ZnO and (●) pure ZnWO₄ calcined at 600 °C for 2 h.

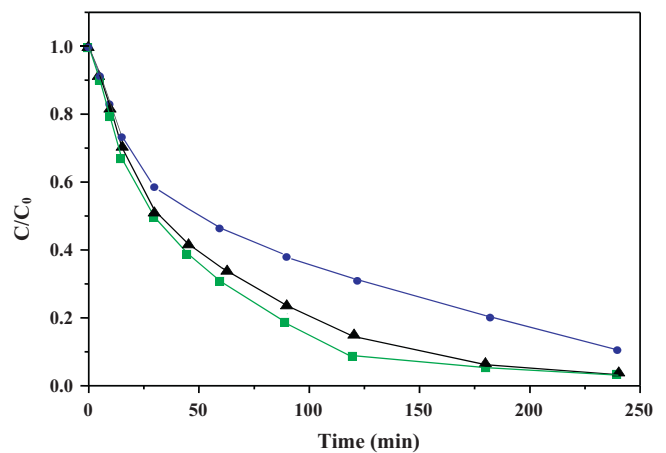


Fig. 8. Photodegradation kinetics of 4-NP over Zn-ZW_{0.25} calcined for 2 h at (●) 500 °C, (■) 600 °C and (▲) 700 °C.

where $E_{MV^{2+}/MV^{+}}^0$ is the standard potential of the redox couple MV^{2+}/MV^{+} equal to -0.445 V vs (NHE) [43]. The values obtained were -0.36 V vs (NHE) for ZnO and -0.14 V vs (NHE) for ZnWO₄.

3.4. Photocatalytic activity

The photocatalytic activity of the powders was investigated by following the degradation of 4-NP under UV light irradiation. Figs. 8 and 9 show the kinetics of photodegradation of 4-NP in the presence of various samples. The degradation rate constant, k , was calculated from the initial slope of the concentration versus time profiles. The k values are reported in Table 2.

Fig. 8 shows the effect of the calcination temperature on the photocatalytic activity of the ZnSn_{0.25} sample. The best efficiency was obtained when the sample was calcined at 600 °C whereas the powders calcined at 500 and 700 °C were less active. As reported by Ohtani et al. [44] for TiO₂ photocatalysts, a high activity should satisfy two requirements: large surface area to adsorb the substrates and high crystallinity to reduce the recombination of the photoexcited electron–hole pairs. The sample calcined at 500 °C has the highest SSA (27.3 m²/g) but it is the least crystalline. Instead, the sample calcined at 700 °C has a high crystallinity but it has a low specific surface area (12.6 m²/g) so that ZnZW_{0.25} calcined at 600 °C was the most active among the three samples.

Fig. 9 shows the kinetics of degradation of 4-NP in the presence of ZnO, ZnWO₄ and mixed ZnO–ZnWO₄ photocatalysts calcined for

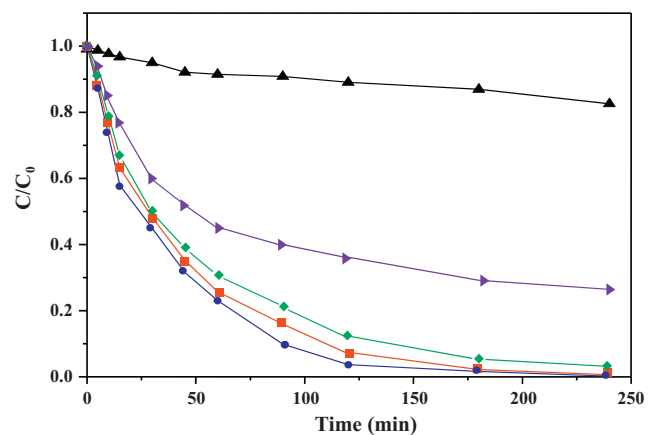


Fig. 9. Photodegradation kinetics of 4-NP over (●) ZnZW_{0.05}, (■) ZnZW_{0.02}, (◆) ZnZW_{0.25}, (▼) pure ZnO and (▲) pure ZnWO₄ calcined at 600 °C for 2 h.

Table 2
Photodegradation rate constants of 4-NP on pure ZnO, pure ZnWO₄ and ZnO–ZnWO₄ photocatalysts.

	ZnO 600 °C/2 h	ZnWO ₄ 600 °C/2 h	ZnZW _{0.02} 600 °C/2 h	ZnZW _{0.05} 600 °C/2 h	ZnZW _{0.25} 500 °C/2 h	ZnZW _{0.25} 600 °C/2 h	ZnZW _{0.25} 700 °C/2 h
$k \times 10^3 \text{ (min}^{-1}\text{)}$	16.5	2.3	33.6	36.3	13.6	25.8	24.8

2 h at 600 °C. The photoactivity of ZnWO₄ was very low compared to that of ZnO but all the ZnO–ZnWO₄ samples were more active than the two pure compounds showing that the contemporaneous presence of ZnO and ZnWO₄ resulted in a synergistic effect. The photocatalytic activity of the mixed samples was found to be related to the ZnO/ZnWO₄ molar ratio and in particular, ZnZW_{0.05} revealed the highest photocatalytic efficiency.

The stability of the ZnO–ZnWO₄ samples was tested by XRD analysis before and after the photoreaction. The intensities of the peaks of ZnO and ZnWO₄ remained practically unchanged indicating the absence of photo-corrosion. Fig. 10 shows the results obtained after reuse of ZnO and ZnZW_{0.05}. Although the degradation efficiency of the mixed sample slightly decreased, ZnZW_{0.05} was again more efficient than ZnO indicating that the ZnO–ZnWO₄ photocatalysts remained effective and reusable under UV light irradiation.

4. Discussion

The experimental results have shown that the photocatalytic activity of ZnO is increased by coupling with ZnWO₄. This enhancement can be explained by the contemporaneous presence of two semiconductors possessing different energy levels for their corresponding conduction and valence bands. Depending on the potentials of the photogenerated holes and electrons, a vectorial transfer of charge carriers from a semiconductor to another is possible, leading to more efficient electron–hole separation and higher photocatalytic activity [10,45].

Both ZnO and ZnWO₄ are n-type semiconductors so that, assuming that the difference between flat band potential and conduction band edge is negligible, it is possible to locate the valence band edge of ZnO and ZnWO₄ by adding the band gap energy to the flat-band potential value. The results have shown that the valence band of ZnO ($E_{VB} = 2.84 \text{ eV}$) is lower than that of ZnWO₄ ($E_{VB} = 3.00 \text{ eV}$). Similarly, the conduction band of ZnO ($E_{CB} = -0.36 \text{ eV}$) is lower than that of ZnWO₄ ($E_{CB} = -0.14 \text{ eV}$). Fig. 11 shows a schematic diagram of the energy band structures of ZnO and ZnWO₄ at pH = 7. Although these data may not be the exact absolute values of the conduction and valence band potentials of ZnO and ZnWO₄, they should offer

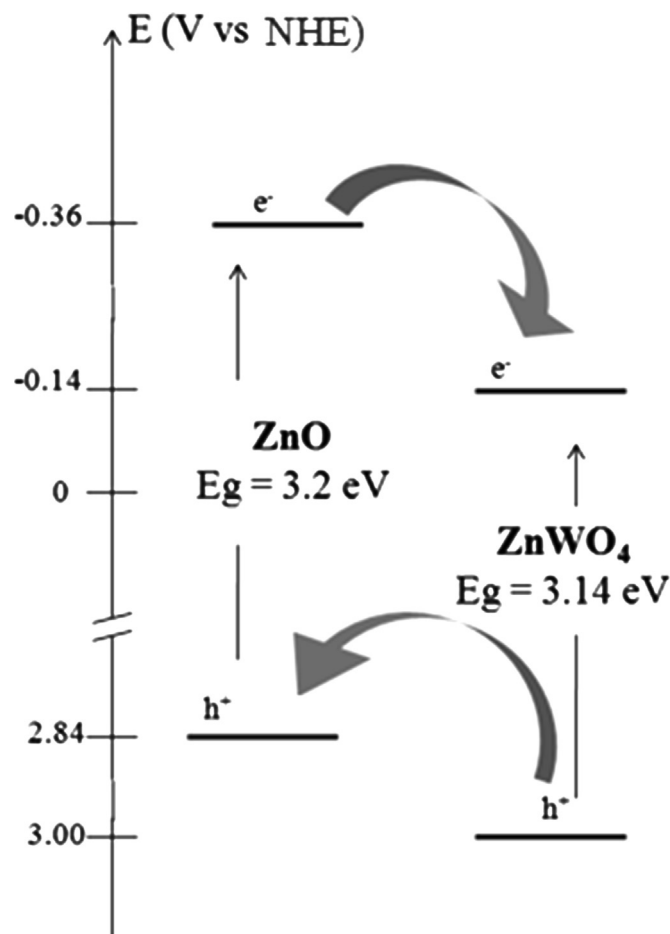


Fig. 11. Schematic diagram representing the charge-transfer processes between coupled ZnO and ZnWO₄ particles.

a correct estimation of the relative band edge positions of the two semiconductors.

When the ZnO–ZnWO₄ nanocomposites are irradiated by UV light, electrons can transfer from the more cathodic conduction band of ZnO to the more anodic conduction band of ZnWO₄. Analogously, holes transfer can occur from the valence band of ZnWO₄ to the valence band of ZnO. The efficient charge separation can increase the lifetime of the charge carriers and enhance the efficiency of the interfacial charge transfer to adsorbed substrates. A mechanistic scheme of the charge separation in the ZnO–ZnWO₄ system is shown in Fig. 11.

The enhanced photoactivity of the ZnO–ZnWO₄ nanocomposites is so attributable to the formation of local heterojunctions between ZnO and ZnWO₄ particles which facilitate the separation of the photogenerated e^-/h^+ pairs. With increase in the content of ZnWO₄ the photoactivity increases due to the an increased number of heterojunctions but it decreases when the content of ZnWO₄ is high probably due to a larger amount of free ZnO₄ particles that are not sufficiently active. Therefore, there is an optimum ZnWO₄ content that leads to a maximum photocatalytic efficiency.

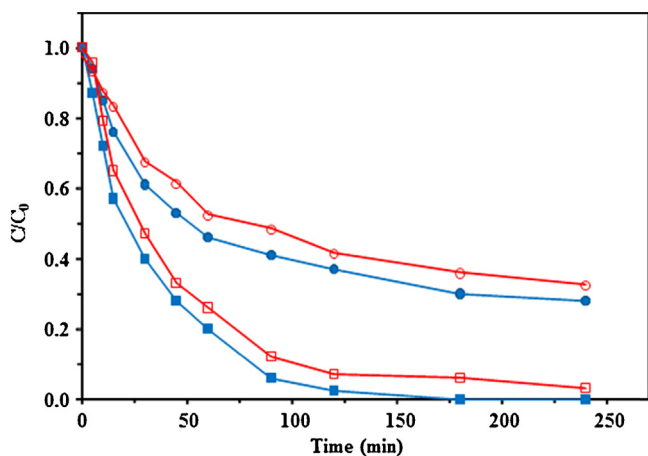


Fig. 10. Reusability tests of (●, ○) ZnO and (■, □) ZnZW_{0.05}. The full symbols refer to the first photocatalytic run, the open symbols to the second one.

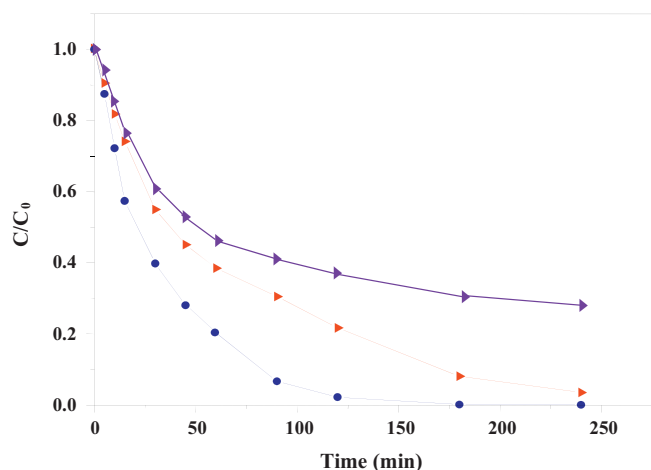


Fig. 12. Photodegradation kinetics of 4-NP over (►) pure ZnO, (●) ZnZW_{0.05} calcined at 600 °C for 2 h and (►) mechanical mixture of ZnO and ZnWO₄.

To verify if the superior activity of the mixed systems was due to the simple coupling of different semiconductors, the photodegradation of 4-NP was also studied in the presence of a mechanical mixture of ZnO and ZnWO₄. Fig. 12 shows a comparison between the results obtained with the ZnZW_{0.05} sample synthesized by the sol-gel method and in the presence of a mechanical mixture with the same composition. The efficiency of this mixture was superior to that of ZnO but lower than that exhibited by the ZnO-ZnWO₄ nanocomposite. This may be explained by assuming that an intimate contact between ZnO and ZnWO₄ particles is necessary for an acceleration of the rate of 4-NP degradation under illumination. Such intimate contact between different particles is easily realized during the sol-gel synthesis of the ZnO-ZnWO₄ nanocomposites while for the mechanical mixture of the powders, there is only a temporary juxtaposition of two distinctly separated phases.

5. Conclusion

ZnO, ZnWO₄ and ZnO-ZnWO₄ nanocomposites were successfully synthesized by a novel sol-gel method followed by calcination. Zn(Ac)₂·2H₂O, H₃PW₁₂O₄₀·xH₂O and methanol were used as the precursors materials. The XRD patterns confirmed the presence of ZnO and ZnWO₄ and the absence of WO₃. The photoefficiency of the ZnO-ZnWO₄ samples was superior to that of pure ZnO or ZnWO₄. The enhanced photoactivity was attributed to the improved charge separation resulting from the coupling of two semiconductors with different energy levels of their conduction and valence bands. The photocatalytic activity was found to be dependent on the calcination temperature and on the ZnO/ZnWO₄ molar ratio. ZnZW_{0.05} revealed the highest efficiency for the degradation of 4-NP.

Acknowledgements

This work was financially supported by MIUR (Rome). HR-TEM experimental data were provided by Centro Grandi Apparecchiature – UniNetLab – Università di Palermo funded by P.O.R. Sicilia 2000–2006, Misura 3.15 Quota Regionale. The authors thank the minister of Higher Education and Scientific Research, Tunisia, for the fellowship awarded to A. Hamrouni.

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