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CTAB-assisted ultrasonic synthesis, characterization and photocatalytic properties of WO₃



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ABSTRACT

WO₃ 2D nanostructures have been prepared by ultrasound synthesis method assisted with CTAB using different molar ratios. The formation of monoclinic crystal structure of WO₃ was confirmed by X-ray powder diffraction (XRD). The characterization of the WO₃ samples was complemented by analysis of scanning electron microscopy (SEM), which revealed morphology mainly of rectangular nanoplates with a thickness of around 50 nm and length of 100–500 nm. Infrared spectroscopy (FI-IR) was used to confirm the elimination of the CTAB in the synthesized samples. The specific surface area was determinate by the BET method and by means of diffuse reflectance spectroscopy (DRS) it was determinate the band-gap energy (E_g) of the WO₃ samples. The photocatalytic activity of the WO₃ oxide was evaluated in the degradation reactions of rhodamine B (rhB) and indigo carmine (IC) under Xenon lamp irradiation. The highest photocatalytic activity was observed in the samples containing low concentration of CTAB with morphology of rectangular nanoplates and with higher surface area value than commercial WO₃. Photodegradation of rhB and IC were followed by means of UV–vis absorption spectra. The mineralization degree of organic dyes by WO₃ photocatalyst was determined by total organic carbon analysis (TOC) reaching percentages of mineralization of 92% for rhB and 50% for IC after 96 h of lamp irradiation.

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1. Introduction

Tungsten oxide (WO₃), an important *n*-type semiconductor, has received wide attention owing to its promising application for electrochromic and photochromic devices, secondary batteries and photocatalysts [1–4]. In this sense, WO₃ has been widely investigated because of its potential application in information displays [5], energy-saving smart windows [6,7], variable-reflectance marrows [8], and photocatalytic [9–11] reactions.

Recently, investigations of WO₃ have been focused on its application as a photocatalyst because of its relatively narrow band-gap energy (less than 3.0 eV). Such a situation allows the use of WO₃ as a novel eco-material for energy renewal, energy storage and environmental cleanup [12]. Because of its ease of preparation, WO₃ has been synthesized via several experimental techniques, such as thermal decomposition [13], acid precipitation [14], solgel [15], hydrothermal synthesis [16] and electrospinning [17], among others. The WO₃ presents the phenomenon of polymorphism, where the monoclinic phase (m-WO₃) has drawn attention

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http://dx.doi.org/10.1016/j.materresbull.2014.10.034 0025-5408/© 2014 Elsevier Ltd. All rights reserved. of scientists and researchers in last decades because it is a more stable phase [18–20]. Furthermore, through these synthesis methods mentioned previously, m-WO₃ is commonly obtained using different experimental conditions, in some cases very specific conditions, making it difficult to obtain. In addition, WO₃ exhibits strong absorption in the visible region at wavelength greater than 480 nm [21], which makes it an attractive candidate for photocatalytic applications under solar irradiation.

Recently, the use of the ultrasound method for the synthesis of semiconductor oxides has received wide attention, which has proved to be an effective technique for generating nanoparticles with attractive properties in a short period of reaction time. The enhanced chemical effect of ultrasound is due to acoustic cavitation phenomena. The major advantage of this method, apart from its fast quenching rate and operation at ambient condition, is that it is a simple and energy efficient process [22]. For this reason, the growing number of publications dealing with ultrasonic irradiation gives an idea about the great potential of the method because of its simplicity and efficiency [23].

On the other hand, in order to control the morphology of the semiconductor oxides, organic additives such as ethylene diamine tetra-acetic acid (EDTA) [24,25] and polyethylene glycol (PEG) [26,27] are commonly added into the reaction system to manipulate the nucleation and growth of the particles. In this

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sense, cetyltrimethyl ammonium bromide (CTAB) assisted by ultrasound technique has emerged as an attractive technique to carry out the synthesis of WO₃ nanostructures. For this reason, in this work the effects of different concentrations of CTAB on the morphologies and photocatalytic properties of WO₃ oxide by ultrasound synthesis method were investigated in the degradation reactions of rhodamine B (rhB) and indigo carmine (IC) in aqueous solution.

2. Experimental

2.1. Synthesis of WO₃ oxide

WO₃ oxide was obtained by ultrasound synthesis method assisted with cetyltrimethyl ammonium bromide (C₁₉H₄₂BrN, CTAB, Sigma-Adrich) in aqueous solution using different molar ration of ammonium tungstate hydrate (H₄₂N₁₀O₄₂W₁₂,xH₂O, 99% purity, Sigma-Aldrich) and CTAB; 1:01, 1:0.25, and 1:0.5. The samples were prepared by the following procedure: 1.65 g $(5.39 \times 10^{-4} \text{ mol})$ of ammonium tungstate hydrate was dissolved in 100 mL of a nitric acid solution (10% v/v, HNO₃) under continuous stirring in an ultrasonic bath ($42 \text{ kHz} \pm 6\%$, 100 W). Afterwards, it was added to the solution a quantity of CTAB of accord to the corresponding molar ration under continuous stirring until the formation of homogeneous solution. Then the solution was maintained without stirring in the ultrasonic bath during 5 h. This step produced a yellow precipitate (hereafter called precursor), which was washed several times with distilled water to neutralize the pH of the solution and finally dried in air at 80°C during 24 h. The precursor was thermally treated at 500 °C from room temperature to the specific temperature with a heating rate of $10 \,^{\circ}$ C min⁻¹ in order to obtain of the WO₃ oxide. For comparative purposes it was used also the commercial WO₃ (99% purity, Fluka) and also the oxide prepared without CTAB.

2.2. WO₃ samples characterization

Structural characterization of WO₃ samples was carried out by X-ray powder diffraction analysis using a BRUKER D2 PHASER diffractometer with CuK α radiation (λ = 1.5418 Å). X-ray diffraction data of the samples was collected in the 2 θ range of 10–70° with a scan rate of 0.02° and 0.2 s⁻¹. Infrared spectroscopy (NICOLET 380 FT-IR) was used to confirm the elimination of the surfactant (CTAB). The morphology and particle size analysis of the samples was investigated by scanning electron microscopy in a FEI Nova 200 NanoSEM.

The band-gap energy (E_g) was determined by means of the UVvis diffuse reflectance absorption spectra of the WO₃ samples, which were taken using a UV-vis spectrophotometer PerkinElmer Lambda 35 equipped with an integrating sphere. The E_g value was calculated for direct transition from the UV-vis spectrum through extrapolating a straight line to the slope of the *x*-axis, using the following equation: $E_g = 1240/\lambda_g$, where, λ_g is the wavelength (nm) of the exciting light and E_g the band gap energy [28]. The BET surface area of WO₃ samples was determined by adsorptiondesorption N₂ isotherms using a BELSORP Mini-II surface area and pore size analyzer. The isotherms were evaluated at $-196 \,^\circ$ C after a degassing of the samples by means of a heat treatment at 150 $\,^\circ$ C for 24 h.

2.3. Photocatalytic experiments

The photochemical reactor employed was a homemade device consisting of a borosilicate glass beaker embedded in a water jacket to maintain the reaction temperature at 25 ± 1 °C. A Xe lamp of

6000-K with a luminous flux of 90500 lux was used as UV and visible-light radiation source.

The photocatalytic activity of WO₃ samples was evaluated in the degradation reactions of rhodamine B (rhB, CAS 81-88-9) and indigo carmine (IC, CAS 860-22-0) in aqueous solution. 200 mL of dye solution containing 200 mg of WO₃ powders were put in a glass beaker and then placed in an ultrasonic bath for 2 min to eliminate aggregates after that the solution was transferred to the reactor. By considering the molar extinction coefficient of the dyes. the initial concentrations were determined to be 5 mg L^{-1} for rhB and 30 mg L^{-1} for IC. The solution was kept in the dark for 1 h in order to ensure that the adsorption-desorption equilibrium of the dye on the catalyst surface has been reached. After this time, the light source was turned on. During the reaction, samples were taken from the reactor at different time intervals, the powders were separated by centrifugation and then the filtered solution was analyzed in a UV-vis spectrophotometer following the procedure established in a previous work [29].

The dyes mineralization degree was examined by analyzing the total organic carbon (TOC) content in solutions using a SHIMADZU TOC-VSCH analyzer. For these experiments were employed 200 mL of the dye solution (50 mg L^{-1} for rhB and 100 mg L^{-1} for IC) containing 200 mg of photocatalyst.

3. Results and discussions

3.1. Structural characterization

The obtained powders of WO₃ with the different molar ratios of ammonium tungstate hydrate and CTAB (1:0.1, 1:0.25, and 1:0.5) were thermally treated at 500 °C. For comparative purposes, the oxide also was prepared without CTAB and thermally treated at same temperature. The materials formed presented a greenish tinge. The X-ray powder diffraction patterns of the WO₃ sample without CTAB (hereafter identified as W500) and with CTAB (hereafter identified as W500) and W0.5-500) are shown in Fig. 1. It was noticed for all samples that the materials crystallized in the monoclinc polymorph of WO₃ according the JCPDS card no. 01-085-0950. All samples presented its main diffraction peaks located at 2θ =23.1, 23.6, 24.3, 26.6, 28.6, 33.3, 34.2, 41.8 and 49.9°, which are well defined and typical of the monoclinic structure.



Fig. 1. X-ray powder diffraction patterns of the WO_3 samples assisted with and without CTAB.



Fig. 2. FT-IR spectra of the WO_3 samples, precursor materials, CTAB, and commercial WO_3 .

Fig. 2 shows the IR spectra for WO₃ samples heated at 500 °C, their precursor materials (W0.1, W0.25, and W0.5), the CTAB and commercial WO₃. The presence of a broad (W-O-W) band, characteristic of WO₃, was observed in synthesized samples to different molar ratios (W0.1-500, W0.25-500, and W0.5-500) at approximately 450, 674, 724, and 855 cm⁻¹, and the same time (W=O) at 950 cm⁻¹. On the other hand, no bands that correspond to O-H, C-H or C-O were observed when the precursors were heated at 500 °C, which indicate that the CTAB was decomposed during this process [30].

3.2. Morphological studies

The morphology and particle size of WO₃ samples were analyzed by SEM. Fig. 3 shows the SEM micrographs of samples obtained by ultrasound irradiation with and without CTAB at 500 °C. When the oxide was prepared without CTAB (W500) were observed particles with heterogeneous morphology in shape of rectangular, square and ovoid nanoplates with a thickness of around 50 nm and length of 100-500 nm (see Fig. 3a). In the samples obtained with CTAB using molar ratio of 1:0.1 and heated at 500 °C (W0.1-500), it was observed more uniform morphology principally of rectangular nanoplates, with a thickness of around 30 nm and length of 100-200 nm (see Fig. 3b). For the samples prepared with molar ratio of 1:0.25 (W0.25-500), it was observed morphology of rectangular nanoplates principally, similar to the samples W0.1-500 but with a length approximately 500 nm as it is shown in Fig. 3c. Although some ovoid particles were also observed to a lesser extent. In the samples with molar ration of 1:0.5 (W0.5-500) it was observed a change in the morphology from rectangular nanoplates to ovoid particles mainly with a size of around 100 nm and irregular shape as it is shown in Fig. 3d. Only the sample W0.5-500 showed different morphology, which is similar to the tendency natural of the commercial WO_3 to form particles of ovoid shape (see Fig. 3e).

Therefore, accordingly to these results we can conclude that the WO₃ samples prepared by ultrasound synthesis method assisted with CTAB presented mainly uniform morphology of rectangular nanoplates with a thickness of around 50 nm and length of 100–500 nm; this morphology was favored by low concentration of CTAB. Whilst with the increase of the CTAB concentration, the morphology of particles gradually change showing a tendency natural to form the morphology characteristic of commercial WO₃.

The change in the morphology of WO₃ oxide by effect of CTAB can be explained as follow: when ammonium tungstate hydrate $(H_{42}N_{10}O_{42}W_{12}.xH_2O)$ was dissolved in distilled water and nitric acid (HNO₃), it was obtained a yellow solution of tungstate acid $(H_2WO_4.xH_2O)$. Then, the solution was maintained in ultrasound bath during a time period causing that the tungstate acid decomposed to produce WO₃ nuclei, containing layers of octahedrons $[WO_6]^{6-}$. The addition of CTAB in the solution provokes the ionization of CTAB into CTA⁺ and Br⁻. In this sense, the CTA⁺ is attracted by the four negatively charged oxygen atoms in the planar surface of $[WO_6]^{6-}$. Therefore, this causes the formation of [CTB-WO₆]²⁻, which orient the planes of the particles to form WO₃ nanoplates [31]. For this reason, the CTAB plays a very important role in the final morphology of the WO₃ powders.

3.3. Band-gap energy and BET surface area analysis

The optical properties of the samples W500, W0.1-500, W0.25-500, and W0.5-500 were analyzed using UV–vis diffuse reflectance spectroscopy. Table 1 shows the band–gap energy (E_g) values of the samples analyzed. The E_g values determined are found in the range reported in the literature (2.5–2.8 eV [32,33]); similar to E_g value of commercial WO₃, which is 2.62 eV.

The specific surface area of WO₃ samples measure by BET method is also incorporated in Table 1. The surface area values of samples prepared with and without CTAB were higher than commercial WO₃. With the increase of the CTAB concentration the specific surface area value decreases. Therefore, the sample with the highest surface area value was W0.1-500. Fig. 4 shows the adsorption–desorption isotherm of WO₃ samples with and without CTAB. In general, a type of profile was observed in all the samples analyzed. The samples (W500, W0.1-500, W0.25-500, and W0.5-500) exhibited typical behavior of a material, which is not porous, or macroporous, respectively (i.e., type II isotherms, according to the classification previously establish for adsorption–desorption–isotherm [34]) as it is observed in Fig. 4a–d.

Therefore, these experiments reveal the modification of surface area of WO_3 oxide by effect of the addition CTAB. This means that at low molar ratios of CTAB, the surface area increases of WO_3 samples. Whilst with a high concentration of CTAB the WO_3 particles tend to agglomerate.

3.4. Evaluation of photocatalytic activity

The photocatalytic activity of the WO₃ samples was evaluated in the degradation reactions of rhB and IC molecules in water under Xe lamp of 6000-K irradiation. Fig. 5 shows the temporal degradation of rhB (5 mg L^{-1}) with the different synthesized WO₃ samples. After 240 min of Xe lamp irradiation it was observed that all samples exhibited better results than sample without CTAB (W500) and commercial WO₃. In general, all the samples were able to bleach the rhB solution in large measure. The best photocatalytic activity was showed by the sample with the low concentration of





Fig. 3. SEM analysis of the morphology of the WO₃ samples obtained by ultrasound synthesis method assisted with and without CTAB: (a) W500, (b) W0.1-500, (c) W0.25-500, (d) W 0.5-500, and (e) commercial WO₃.

CTAB (W0.1-500), i.e., the sample that presented the highest surface area value and consequently the mainly morphology of rectangular nanoplates.

Fig. 6 shows the photocatalytic activity of WO₃ with and without CTAB in the degradation of IC (30 mg L^{-1}) . It is observed higher activity than with the rhB although the initial IC

concentration was 6 times higher. This is due to their respective molar extinction coefficients. All the samples presented better activity than the sample without CTAB and commercial WO₃. After 120 min of exposure under Xe lamp the samples with CTAB (i.e., W0.1-500, W0.25-500, and W0.5-500) were able to bleach in almost 100% the IC solution. The WO₃ sample that showed the best

Table 1

Physical properties of the WO₃ samples synthesized under different experimental conditions.

Method	Morphology	Test conditions	Photocatalytic activity	Reference
Precipitation in ethanol solution	The particles tend to form large agglomerates formed by small particles (100 nm) and of irregular shapes	35 W Xe lamp.Batch typereactor.1:1	68%	[11]
Microwave-assisted hydrothermal	Ovoid morphology with particles sizes between 20 and 50 nm	(catalyst:rhB solution)	88%	[37]
Ultrasound assisted CTAB	Morphology of rectangular nanoplates with a thickness of around $50nm$ and length of 100-500nm		100%	This work

activity was the W0.1-500, i.e., the sample that exhibited a more uniform morphology of rectangular nanoplates and the smallest size. In fact it is the sample that presented highest surface area value. In this sense, it can be observed that increasing the surface area of the WO₃ samples increases the degradation rates of rhB and IC (see Fig. 7).

It is well known that surface area play a determinant role in the photocatalytic properties. In this sense, high surface area values generate more active sites and high reaction rates of photogenerated electron-hole pairs on the surface of photocatalyst to interact with the reaction medium. Such a situation provokes an increase in the efficiency of photocatalytic processes. In the same way, other factor that favors the activity of WO₃ samples is the morphology of rectangular nanoplates, which was favored at low concentration of CTAB. Whilst a high concentration of CTAB the WO₃ particles are agglomerated to obtain a morphology of ovoid particles principally. Therefore, these experiments reveal that the factors governing the photocatalytic activity of the WO₃ samples in this work are principally the morphology of rectangular nanoplates, specific surface area and addition of CTAB in low concentration.

On the other hand, for comparison purpose it was selected the sample that presented the best activity (W0.1-500) and its photocatalytic activity was compared against TiO₂ (P25) in the degradation of rhB and IC under the same experimental conditions. Fig. 8 shows the temporal degradation of rhB (a) and IC (b) with WO₃ against TiO₂. It was observed that WO₃ presented a photocatalytic activity similar to TiO₂ for rhB solution after 240 min under Xe lamp irradiation (bleach about of 90%). Whilst for IC solution, the WO₃ synthesized in this work showed an activity higher than TiO₂ after 120 min under Xe lamp irradiation. These results corroborated the potential of WO₃ synthesized by ultrasound method assisted with CTAB as photocatalyst in the degradation of organic compounds, even showing better photocatalytic activity than TiO₂ (P25), in particular for the degradation of IC.

Fig. 9 shows the UV–vis absorption spectra when rhB and IC are photodegraded by a WO_3 sample used as photocatalyst (W0.1-500); it is the sample that exhibited the best photocatalytic properties. Accordingly to the UV–vis absorption spectra it is assumed the complete degradation of rhB via a direct attack to the aromatic rings of its molecule [35], which leads to the breaking of



Fig. 4. N₂ adsorption-desorption isotherms of the WO₃ samples prepared by ultrasound synthesis method assisted with and without CTAB: (a) W500, (b) W0.1-500, (c) W0.25-500, (d) W 0.5-500.



Fig. 5. Changes in the rhB concentration $(5 \,\text{mg}\,\text{L}^{-1})$ during its photocatalytic degradation in the presence of WO₃ under different experimental conditions; a Xe lamp was used as source of radiation, pH 6.0. The concentration of rhB was determined through its maximum absorption band (554 nm).

the bonds and thus provokes the degradation of the dye (see Fig. 9a). In the case of IC, it is assumed almost a complete degradation via a direct attack to the molecule of IC breaking its C=C bond to yield isatin 5-sulfonic acid as the main aromatic product [36]. This leads to the breaking of the molecule and thus causes the degradation of the dye (see Fig. 9b).

To determine if it is feasible the mineralization of organic dyes and discard that only the dyes solution is being bleached for WO_3 oxide exposed under Xe lamp irradiation. It was determinate the mineralization degree by means of total organic carbon (TOC) content of the photocatalytic test in the degradation reactions of rhB and IC (see Fig. 10). For these experiments it was used the W0.25-500 sample as photocatalyst for rhB and the W0.1-500 sample for IC, which have the lowest and highest surface area, respectively. After 96 h under lamp irradiation the mineralization degree reaches almost 92% for rhB and 50% for IC, therefore it is concluded that using WO₃ synthesized by ultrasound method



Fig. 6. Changes in the IC concentration (30 mg L^{-1}) during its photocatalytic degradation in the presence of WO₃ under different experimental conditions; a Xe lamp was used as source of radiation, pH 6.0. The concentration of IC was determined through its maximum absorption band (610 nm).



Fig. 7. Effect of surface area of the WO_3 samples against the degradation rates of rhB after 240 min and IC after 120 min.

assisted with CTAB as photocatalyst it is possible to provoke a high mineralization degree of organic dyes. These results were associated with the UV–vis absorption spectra previously explained, where it was observed that it is feasible the complete degradation of rhB and almost the complete degradation of IC. Therefore, these results confirm that it is feasible to break the bond



Fig. 8. Photocatalytic activity of WO₃ against TiO₂ (P25) in the degradation of: (a) rhB (5 mg L⁻¹) and (b) IC (30 mg L⁻¹) under same experimental conditions; a Xe lamp was used as source of radiation, pH 6.0.



Fig. 9. Variation of the UV–vis absorption spectra during the photocatalytic degradation of: (a) rhB and (b) IC in presence of one of the samples that exhibited the best activity (W0.1–500).

of organic compounds (rhB and IC) during the photocatalytic reactions.

Unlike the previous work [11,37], this work involved the successful preparation of WO_3 nanoplates by ultrasound synthesis method assisted with CTAB. In conclusion it was observed that the addition of low concentration of CTAB in the synthesis favors the formation of WO_3 with morphology of rectangular nanoplates, increasing the surface area and consequently exhibiting high photocatalytic activities in the degradation reactions of rhB and IC. Therefore, this synthesis method can be an alternative route to



Fig. 10. Variation of the TOC during the mineralization of rhB and IC under a Xe lamp irradiation, pH 6.0.

Table 2

Photocatalytic degradation of rhB (5 mg L^{-1}) using WO₃ synthesized by different methods under irradiation Xenon lamp during 3 h.

Sample	$E_{g}(eV)$	BET surface area $(m^2 g^{-1})$
Commercial	2.6	3.3
W500	2.5	4.4
W0.1-500	2.6	8.7
W0.25-500	2.6	5.9
W0.5-500	2.6	6.2

prepare other materials using CTAB in order to modify its morphology and specific surface area, allowing an improvement on its photocatalytic properties in the degradation reaction of organic compounds.

Also it is important to mention that in previous studies we have obtained only morphology of ovoid particles by different methods of synthesis and reported that the photocatalytic properties were mainly associated to the material crystallinity [11,37]. In this sense, a comparative study of WO₃ obtained by different synthesis methods used as photocatalyst in the degradation reaction of rhB under same conditions is shown in Table 2. It is observed that morphology depends strongly of the synthesis method and it is an important factor in the photocatalytic applications. In conclusion, the WO₃ with morphology of rectangular nanoplates presented the better photocatalytic activity; this material was synthesized by ultrasound method assisted with CTAB.

Therefore, in this work it is important to stand out that it was obtained WO_3 powders mainly with morphology of rectangular nanoplates and that the photocatalytic activity was attributed principally to the morphology, specific surface area, and the presence of CTAB.

4. Conclusions

WO₃ 2D nanostructures with morphology of rectangular nanoplates were successfully synthesized by ultrasound method assisted with CTAB. The morphology of the WO₃ undergoes a transition from rectangular nanoplates to ovoid particles by effect of the increase in the addition of CTAB. The specific surface area of all the synthesized samples was higher than commercial WO₃. The highest surface area value was obtained for the sample synthesized with the lowest concentration of CTAB. All the synthesized samples used as photocatalysts showed better photocatalytic activity than the commercial WO₃ in the degradation reactions of rhB and IC in aqueous solution under Xe lamp irradiation. The sample that showed the best photocatalytic activity was obtained with the low concentration of CTAB (W0.1-500), i.e., the sample that presented highest surface area value and the morphology mainly of rectangular nanoplates, even showing better activity than TiO₂ (P25) in the degradation of IC and a similar result with the rhB. The photocatalytic activity of WO3 oxide was attributed to the morphology of rectangular nanoplates, specific surface area, and the addition of CTAB. The almost complete mineralization it was achieved after 96 h under Xe lamp irradiation of the organic dyes, 92% for rhB and 50% for IC. This synthesis method can be feasible to prepare other materials with the addition of CTAB for modify its morphology, increasing the specific surface area and improving its photocatalytic properties in the degradation reaction of organic compounds.

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References

- [1] G.R. Bamwenda, H. Arakawa, The visible light induced photocatalytic activity
- of tungsten trioxide powders, Appl. Catal. A 210 (2001) 181–191. [2] X.F. Cheng, W.H. Leng, D.P. Liu, J.Q. Zhang, C.N. Cao, Enhanced photoelectrocatalytic performance of zn-doped WO₃ photocatalysts for nitrite ions degradation under visible light, Chemosphere 68 (2007) 1976-1984.
- [3] S.J. Hong, H. Jun, P.H. Borse, J.S. Lee, Size effect of WO_3 nanocrystals for photooxidation of water in particulate suspension and photoelectrochemical film systems, Int. J. Hydrogen Energy 34 (2009) 3234-3242.
- [4] R. Huang, Y. Shen, L. Zhao, M. Yan, Effect of hydrothermal temperature on structure and photochromic properties of WO₃ powder, Adv. Powder Technol. 23 (2012) 211-214.
- [5] C. Avellaneda, L. Bulhoes, Photocromic properties of WO₃ and WO₃:X (X = Ti, Nb, Ta, and Zr) thin films, Solid State Ionics 165 (2003) 117-121.
- [6] R. Baetens, B.P. Jelle, A. Gustavsen, Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings; a state-of the-art-review, Sol. Energy Mater. Sol. Cells 94 (2010) 87-105.
- [7] C.G. Granqvist, S. Green, G.A. Niklasson, N.R. Mlyuka, S. Von Kraemer, P. Georén, Advances in chromogenic materials and devices, Thin Solid Films 518 (2010) 3046-3053
- [8] K. Tajima, Y. Yamada, S. Bao, M. Okada, K. Yoshimura, Characterization of flexible switchable mirror film prepared by DC magnetron sputtering, Vacuum 84 (2010) 1460-1465.
- [9] B. Subash, B. Krishnakumar, V. Pandiyan, M. Swaminathan, M. Shanthi, Synthesis and characterization of novel WO3 loaded Ag-ZnO and its photocatalytic activity, Mater. Res. Bull. 48 (2013) 63-69.
- [10] G. He, C. Liang, Y. Ou, D. Liu, Y. Fang, Y. Xu, Preparation of novel Sb₂O₃/WO₃ photocatalysts and their activities under visible light irradiation, Mater. Res. Bull. 48 (2013) 2244-2249.
- [11] C. Gómez-Solís, D. Sánchez-Martínez, I. Juárez-Ramírez, A. Martínez-de la Cruz, Leticia M. Torres-Martínez, Facile synthesis of m-WO3 powders via precipitation in ethanol solution and evaluation of their photocatalytic activities, J. Photochem. Photobiol. A 262 (2013) 28-33.
- [12] H. Wang, P. Xu, T. Wang, The preparation and properties study of photocatalytic nanocrystalline/nanoporous WO₃ thin films, Mater. Des. 23 (2002) 331-336.
- [13] H. Yan, X. Zhang, S. Zhou, X. Xie, Y. Lou, Y. Yu, Synthesis of WO₃ nanoparticles for photocatalytic O2 evolution by thermal decomposition of ammonium tungstate loading on g- C₃N₄, J. Alloys Compd. 509 (2011) L232-L235.
- [14] J. Huang, X. Xu, C. Gu, G. Fu, W. Wang, J. Liu, Flowe-like and hollow sphere-like WO₃ porous nanostructures: selective synthesis and their photocatalysis property, Mat. Res. Bull. 47 (2012) 3224-3232.
- [15] W. Wang, Y. Pang, S. Hodgson, XRD studies of thermally stable mesoporous tungsten oxide synthesized by a template sol-gel process from tungstic acid precursor, Micropor. Mesopor. Mater. 121 (2009) 121-128.
- [16] R. Huirache, F. Paraguay, M.A. Albiter, J. Lara, R. Martinez, Synthesis and characterization of WO₃ nanostructures prepared by an aged-hydrothermal method, Mater. Charact. 60 (2009) 932-937.
- [17] X. Lu, X. Liu, W. Zhang, C. Wang, Y. Wei, Large-scale synthesis of tungsten oxide nanofibers by electrospinning, J. Colloid Interface Sci. 298 (2006) 996-999.
- [18] D. Chen, L. Gao, A. Yasumori, K. Kuroda, Y. Sugahara, Size and shape controlled conversion of tungstate based inorganic-organic hybrid belts to WO3 nanoplates with high specific surface areas, Small 4 (2008) 1813-1822.

- [19] X. Shen, G. Wang, D. Wexler, Large-scale synthesis and gas sensing application of vertically aligned and double-sided tungsten oxide nanorod arrays, Sens. Actuators B 143 (2009) 325-332.
- [20] D.J. Ham, A. Phuruangrat, S. Thongtem, J.S. Lee, Hydrothermal synthesis of monoclinic WO₃ nanoplates and nanorods used as an electrocatalyst for hydrogen evolution reactions from water, Chem. Eng. J. 165 (2010) 365-369.
- [21] K. Sayama, H. Hayashi, T. Arai, M. Yanagida, T. Gunji, H. Sugihara, Highly active WO3 semiconductor photocatalyst prepared prepared from amorphous perotungstic acid for the degradation of various organic compounds, Appl. Catal. B 94 (2010) 150-157.
- [22] J. Guo, S. Zhu, Z. Chen, Y. Li, Z. Yu, J. Li, C. Feng, D. Zhang, Sonochemical synthesis of TiO₂ nanoparticles on graphene for use as photocatalyst, Ultrason. Sonochem. 18 (2011) 1082.
- [23] E. Ohayon, A. Gedaken, The application of ultrasound radiation to the synthesis of nanocrystalline metal oxide in a non-aqueous solvent, Ultrason. Sonochem. 12 (2010) 173–178.
- [24] G.R. Li, C.R. Dawa, B. Qetal, Electrochemical self-assembly of ZnO nanoporous structures, J. Phys. Chem. C 111 (2007) 1919-1923.
- [25] W.L. Wojciech, Systematic study of hydrothermal crystallization of zinc oxide (ZnO) nano-sized powders with superior UV attenuation, J. Cryst. Growth 312 2009) 100-108.
- [26] J.X. Duan, X.T. Huang, E.K. Wang, PEG-assisted of ZnO nanotubes, Mater. Lett. 60 (2009) 1918–1921.
- [27] L.R. Toib, K. Zohar, M. Alagem, Y. Tsur, Synthesis of stabilized nano-particles of zinc peroxide, Chem. Eng. J. 136 (2008) 425-429.
- [28] N. Rungjaroentawon, S. Onsuratoom, S. Chavadej, Hydrogen production from water splitting under visible light irradiation using sensitized mesoporousassembled TiO₂-SiO₂ mixed oxide photocatalysts, Int. J. Hydrogen Energy 37 (2012) 11061-11071.
- [29] A. Martinez-de la Cruz, S. Obregón, Synthesis and characterization of nanoparticles of α -Bi₂Mo₃O₁₂ prepared by co-precipitation method: Langmuir adsorption parameters and photocatalytic properties with rhodamine B, Solid State Sci. 11 (2009) 829-835.
- [30] R. Viajayalakshmi, M. Jayachandran, C. Sanjeeviraja, Structural, electrochromic and FT-IR studies on electrodeposited tungsten trioxide films, Curr. Appl. Phys. 3 (2003) 171–175.
- [31] O. Yayapao, T. Thongtem, A. Phuruanfrat, S. Thongtem, CTAB-assisted hydrothermal synthesis of tungsten oxide microflowers, J. Alloys Compd. 509 (2011) 2294-2299.
- [32] X.F. Cheng, W.H. Leng, D.P. Liu, J.Q. Zhang, C.N. Cao, Enhanced photoelectrocatalytic performance of Zn-doped WO3 photocatalysts for nitrite ions degradation under visible light, Chemosphere 68 (2007) 1976-1984.
- [33] S.J. Hong, H. Jun, P.H. Borse, J.S. Lee, Size effects of WO₃ nanocrystals for photooxidation of water in particulate suspension and photoelectrochemical film systems, Int. J. Hydrogen Energy 34 (2009) 3234–3242.
- [34] J.B. Condon, Surface Area and Porosity Determinations by Physisorption: Measurements and Theory, 1st ed., Elsevier, Netherlands, 2006.
- [35] M.A. Behnajady, N. Modirshahla, S.B. Tabrizi, S. Molanee, Ultrasonic degradation of rhodamine B in aqueous solution: influence of operational parameters, J. Hazard. Mater. 152 (2008) 381-386.
- [36] C. Flox, S. Ammar, C. Arias, E. Brillas, A.V. Vargas-Zavala, R. Abdelhedi, Electro-Fenton and photoelectro-fenton degradation of indigo carmine in acidic aqueous medium, Appl. Catal. B 67 (2006) 93-104.
- [37] Diana B. Hernandez-Uresti, D. Sánchez-Martínez, A. Martínez-de la Cruz, S. Sepúlveda-Guzmán, Leticia M. Torres-Martínez, Characterization and photocatalytic properties of hexagonal and monoclinic WO₃ prepared via microwave-assisted hydrothermal synthesis, Ceram. Int. 40 (2014) 4767-4775.