



Optimization of the photocatalytic activity of CdO + CdTiO₃ coupled oxide thin films obtained by sol–gel technique

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ABSTRACT

In the preparation of CdO + CdTiO₃ polycrystalline thin films by the sol–gel method, the optical, structural and crystalline properties, as well as the photocatalytic activity (PA) depends strongly on the sintering temperature (Ts) of the films and of the Ti/Cd ratio used in the precursor solution. In this work, CdO + CdTiO₃ thin films were prepared using a Ti/Cd constant ratio in the precursor solution. The films were sintered at six different Ts in the 450–550 °C range, in an open atmosphere. The structure of the films was characterized by X-ray diffraction and the PA was evaluated by the photobleaching of methylene blue in an aqueous solution using a UV–vis spectrometer. The relative intensity of the diffraction peaks associated with CdO and CdTiO₃, change with the Ts. The better photocatalytic activities were obtained for the films sintered at 490 °C and 550 °C. When the CdO was removed from the films by chemical etching the PA decreased, showing the importance of coupling both oxides.

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1. Introduction

In recent years, a very promising treatment based on the oxidation of hazardous organic compounds is the heterogeneous photocatalysis [1]. One of the main materials used for this application is titanium dioxide (TiO₂), however, other oxides exist which have been tested as photocatalysts. For example, some studies have confirmed that zinc oxide (ZnO) exhibits a better efficiency than TiO₂ in the photocatalytic degradation of dyes in aqueous solutions [2] and in the oxidation of protocatechuic acid [3]. Beside, cadmium oxide (CdO) is useful for oxidation of aniline [4]. Even when the Cd is toxic and poisonous to humans and the environment, CdO material requires high temperature for the Cd evaporation [5]. CdO thin films have been synthesized by various techniques with several applications. In this way, it is important to study different compounds as catalysts, due to the fact that some of ones can be good for degrading an organic compound, but not good for others ones.

The efficiency in a photocatalytic reaction depends on different factors. One of them, the most critical, is the high recombination probability of the electron–hole pair (e⁻–h⁺) in the bulk and on the surface of the semiconductor oxide [6]. In order to decrease this recombination rate, the coupled oxide systems (COS) can be an important alternative [6]. COS are obtained starting from multicomponent oxide thin films. When two crystalline grains of

different oxides are in contact, the photo-generated e⁻–h⁺ pair in one grain is spatially separated by a built electric field in the shared interface and because carriers from one of the phase find lower energy levels in the other phase in contact, avoiding the recombination. The electric field is due to the difference of the band gaps and electronic affinities between neighboring grains. In Fig. 1, as a general example, the small circle represents a crystalline grain of cadmium sulfide (CdS), while the big circle is a crystalline grain of a metal oxide of bigger band gap (MO) than CdS semiconductor [7]. When the material is illuminated with enough energy, the photons are absorbed and produce the generation of e⁻–h⁺ pairs. Due to that, the conduction band (CB) of the CdS, which is energetically located above the CB of the MO, the photo-generated electrons from the CdS are carried onto the MO, while the holes from the valence band (VB) are carried onto the CdS. Through this mechanism, the photo-generated e⁻–h⁺ pairs are spatially separated leading to an increase of the efficiency of the photocatalytic process.

In this work, multicomponent oxide thin films formed by CdO and cadmium titanate (CdTiO₃) were prepared by sol–gel. The Ti/Cd ratio and the Ts range were selected considering previous works reported by the authors [8,9], in order to optimize the photocatalytic activity of CdO + CdTiO₃ films, and also to show the importance of the COS. The crystalline quality and the relative intensity of the peaks associated with CdO and CdTiO₃ change with the Ts, finding the better photocatalytic activities for the films with Ts of 490 and 550 °C. When the CdO was removed from the films by chemical etching (CE), the PA decreased, showing the importance of the band gap coupling of both oxides.

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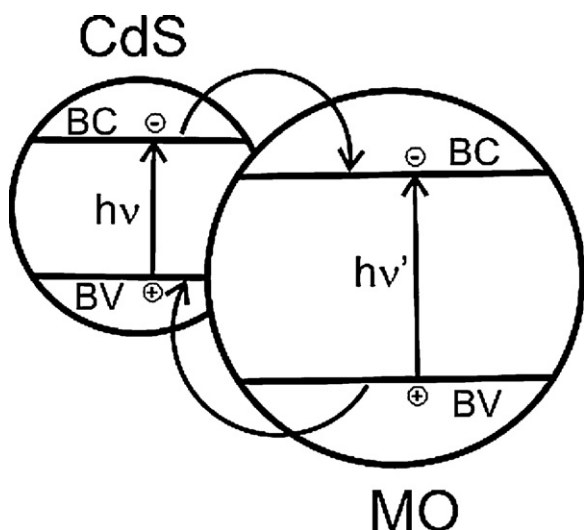


Fig. 1. Diagram illustrating the principle of charge separation in the CdS–MO coupled semiconductor system. MO is a metal oxide with bigger band gap than CdS.

2. Experimental details

2.1. The solution

The TiO₂ precursor solution was prepared starting from the following reagents: for 1 mol of titanium isopropoxide (TIP), 36.46 mol of ethanol, 0.4692 mol of nitric acid, and 5 mol of deionized water were used. Ethanol was divided into two equal parts: one used for the TIP dissolution, and the other one mixed with both water and acid. Both solutions were prepared around 0 °C using an ice water bath; afterwards, they were mixed under magnetic stirring at 0 °C. The mixture was maintained at this temperature. The CdO precursor solution was obtained by means of the following procedure: 1 mol of cadmium acetate dehydrate (Cd(CH₃COO)₂·2H₂O) was dissolved in 23 mol of methanol, afterwards, 0.2 mol of glycerol was added. A separate solution consisting of 23 mol of methanol and 0.5 mol of triethylamine was incorporated in the first solution at room temperature. Finally, both precursor solutions (CdO and TiO₂) were mixed at 0 °C under magnetic stirring, at a Ti/Cd ratio of 0.67. The final solution was transparent and free of particles.

2.2. The films

The films were deposited at room temperature by the dipping method 24 h after the preparation of the final solution, on glass substrates. The withdrawal speed was 3.0 cm/min. The samples were thermally pre-heated at 100 °C for 60 min and then sintered in the Ts interval of 450–550 °C in steps of 20 °C for 60 min. Ts was maintained with an accuracy of ±2 °C during the sintering. The samples were kept inside the oven until room temperature was reached. The preheated and sintered treatments were done in an open atmosphere. All the films studied were obtained by a five-dipping procedure. The X-ray diffraction (XRD) patterns were registered using a Rigaku D/max-2100 diffractometer (Cu K α radiation, 1.5406 Å), using a thin film attachment. The UV–vis transmission spectra were obtained on a Perkin-Elmer Lambda-2 spectrophotometer with a blank piece of glass substrate in the reference beam.

2.3. The PA characterization

The PA was quantified by means of the photobleaching of methylene blue (MB) in aqueous solution. 3 ML of a MB solution

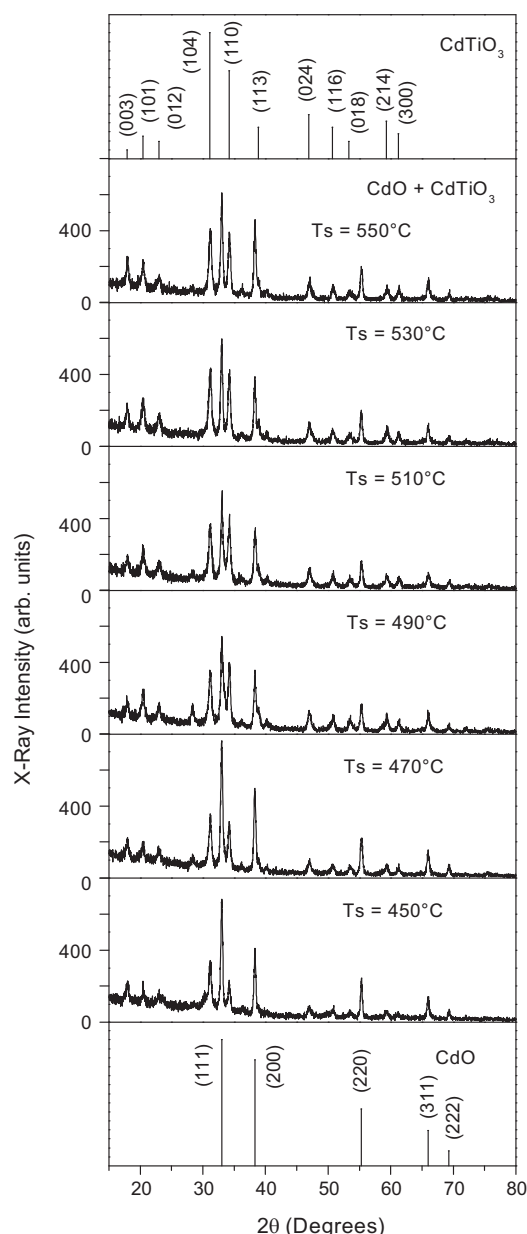


Fig. 2. XRD patterns of CdO + CdTiO₃ films deposited at different sintering temperatures.

at initial concentration of 2.5×10^{-5} mol/L was put in a quartz cell of dimension 1 cm × 1 cm × 4 cm. A sample of rectangular geometry (area = 1.75 cm²) was immersed into the cell and this arrangement (cell + solution + sample) was exposed to UV light. A G15T8 germicidal lamp with power of 15 W was used as the UV source. The distance between cell and lamp was 4 cm and the exposure times were from 1 to 5 h. During the exposure time the temperature was constant (at room temperature). The MB residual concentration ([MB]) was determined starting from absorbance measurements using an Agilent UV–vis spectrometer, model 8453.

3. Results and discussion

XRD patterns (Fig. 2) show that the films are polycrystalline. In all temperatures of the range studied the films are constituted of two oxides: the CdO in its cubic phase and the CdTiO₃ in its ilmenite phase. As can be seen from the figure, the relative intensities of both phases change with the Ts. At 450 °C, the XRD pattern shows mainly

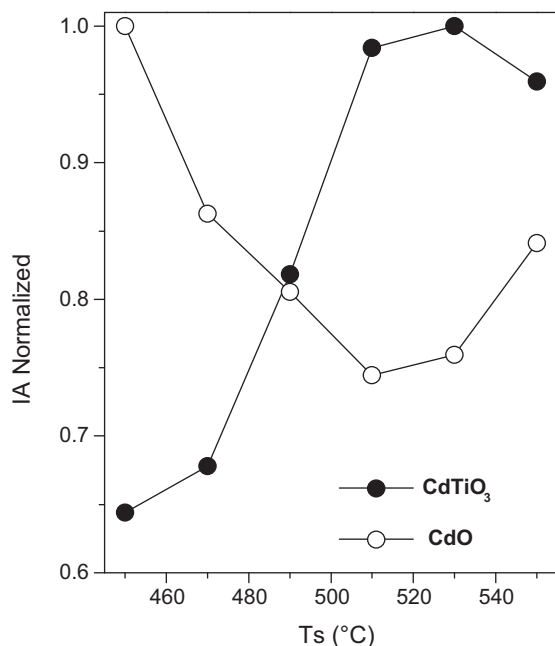


Fig. 3. Normalized integrated area (IA) for each phase, as a function of the sintering temperature.

the peaks associated with the CdO, but, when the Ts increases, the intensity of the peaks corresponding to the CdTiO₃ increases with respect to the ones of the CdO. In Fig. 3, the normalized integrated area (IA) for each compound, as a function of the Ts is shown. As IA is

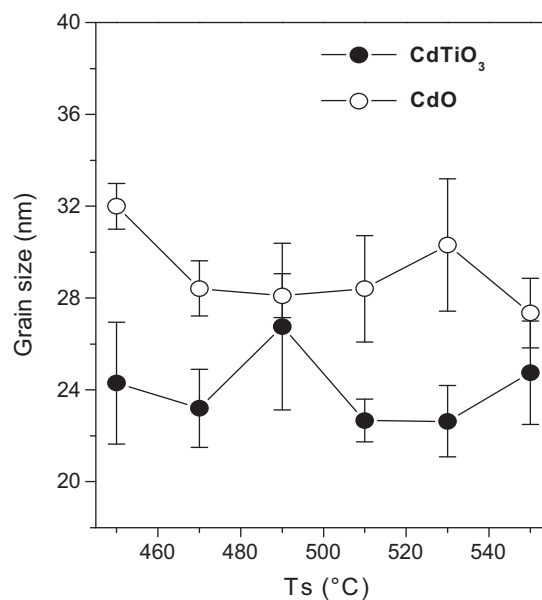


Fig. 4. CdO and CdTiO₃ grain sizes as a function of the sintering temperature.

proportional to the amount of diffracted material, we can say that when Ts is increased the amount of CdTiO₃ increases at expense of the crystallization of both CdO and TiO₂, in amorphous phase. For the highest Ts's (530 °C and 550 °C), the amount of CdO starts to increase. The grain size (GS) was calculated from the Scherrer's formula (Fig. 4). As can be seen, the GS is nearly constant for both

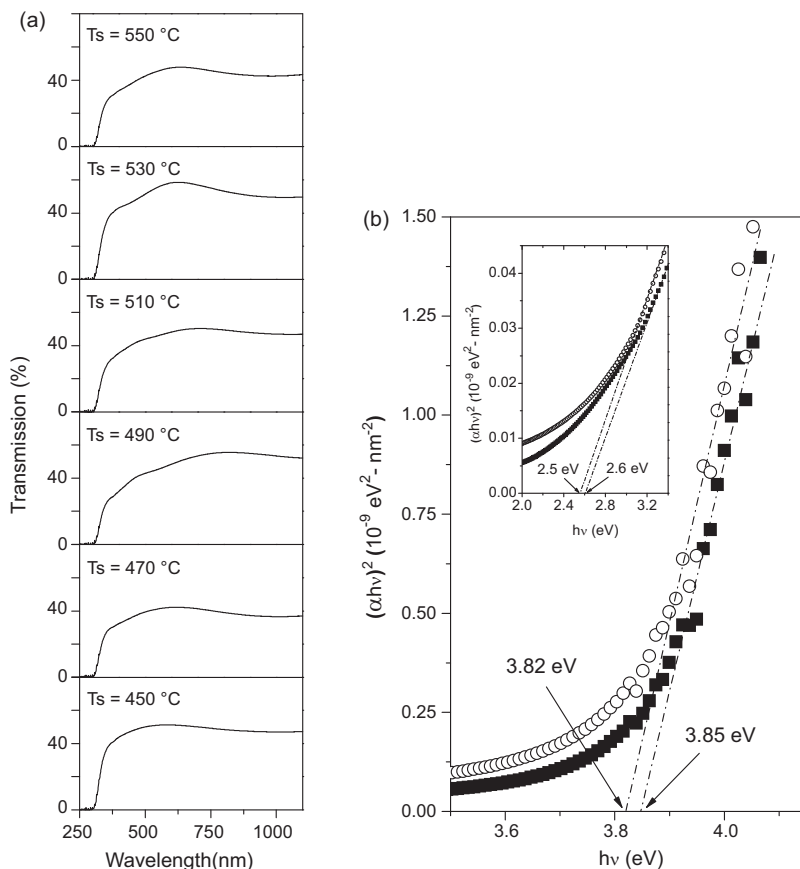


Fig. 5. (a) Optical transmission spectra of CdO + CdTiO₃ films for each of Ts studied. (b) Band gap energy values calculated for the films constituted of the compound of CdTiO₃ (3.8 eV) and CdO (2.5 eV) (inset). Films sintered at 450 °C (○) and 550 °C (■).

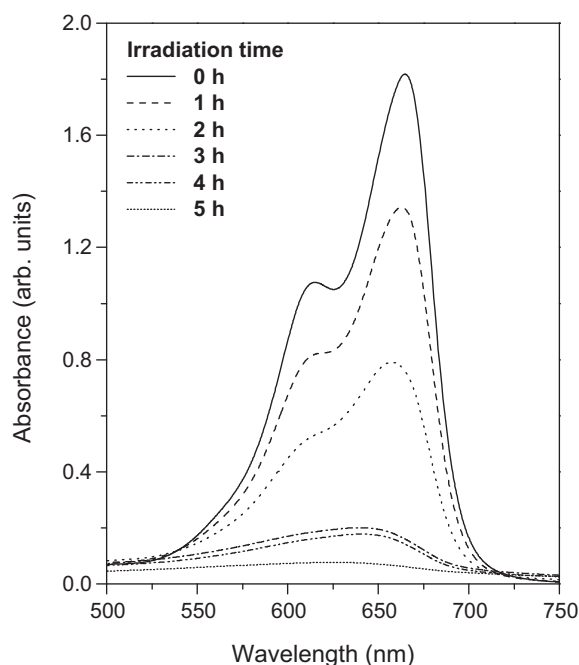


Fig. 6. MB absorption spectra of films with $T_s = 490^\circ\text{C}$ at different times of irradiation.

phases for all temperatures of the range studied, around 24 nm and 29 nm for CdO and CdTiO₃, respectively. However, at $T_s = 490^\circ\text{C}$ and 550°C , the GS values of both phases are very similar.

In Fig. 5(a), the optical transmission spectra are shown for each of T_s studied. In general, the films are opaque indicating that the surface of all the films is rough and consequently the transmission is relatively low. As can be seen from the figure, the absorption edge (AE) seems to have contributions from the two component oxides CdO and CdTiO₃. Direct energy band gap (BG) for the ilmenite phase CdTiO₃ of 3.9 eV was previously reported by us [9] and for perovskite-CdTiO₃ single crystals made by Yakubovskii et al. a value of 3.35 eV [10]. On the other hand, it is known that the CdO has one BG at 2.5 eV (direct) and another at 2.0 eV (indirect) [11]. Fig. 5(b) shows the band gap energy (E_g) calculated for shorter λ 's (higher $h\nu$ values), which correspond to the compound of higher band gap (CdTiO₃). The inset of the same figure shows the E_g for larger λ 's (lower $h\nu$'s), which correspond to the compound of lower band gap (CdO). We think that this fact is due to aggregates of CdO and CdTiO₃ crystalline grains are formed separately, similar to islands of each material.

In Fig. 6 are shown the MB absorption spectra, in the 500–750 nm range, obtained after 1, 2, 3, 4 and 5 h of UV irradiation for the sample sintered at $T_s = 490^\circ\text{C}$. The spectrum of the [MB] initial ($t = 0$) is also included. It is observed that the intensity of the absorption bands (which is equivalent to [MB]), decreases as the irradiation time increases. Starting from these absorption spectra, the [MB] normalized as a function of the time (h) and for three different T_s (450, 490 and 550°C), is shown in Fig. 7. As can be seen, the [MB] vs. time has an exponential decay, characteristic of a first order reaction:

$$[\text{MB}] = [\text{MB}]_0 e^{-kt}$$

where k is the rate constant, $[\text{MB}]_0$ is the initial MB concentration ($=1$), and t is the time. By means of a fitting to exponential decay, the rate constant was evaluated for all the samples. In Fig. 8 is shown the k (h^{-1}) values as a function of T_s . As can be seen from the figure, the best photocatalytic activities were for the samples sintered at 490°C and 550°C with k values of 0.7 and 0.72 h^{-1} respectively.

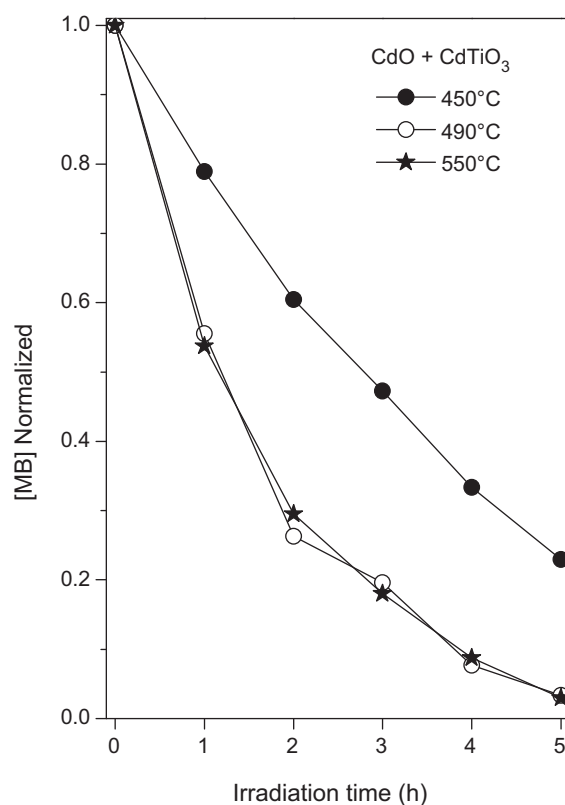


Fig. 7. [MB] normalized as a function of the time for three different sintering temperatures.

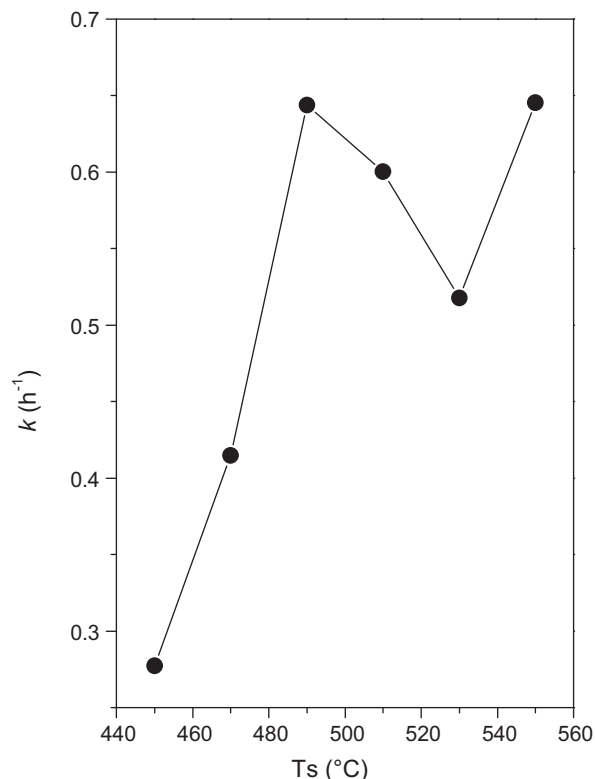


Fig. 8. Rate constant (k) values as a function of sintering temperature.

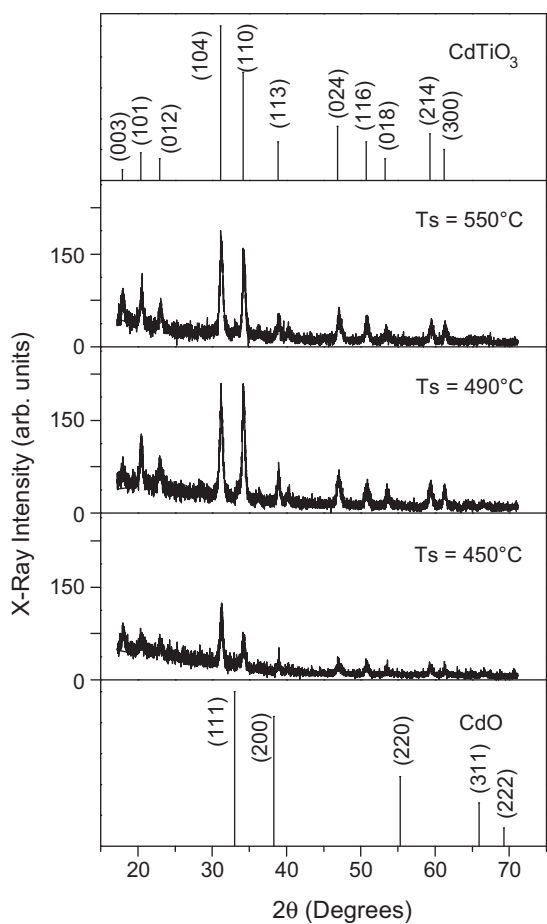


Fig. 9. XRD patterns of the films sintered at three different sintering temperatures, after a chemical etching.

These values are inside of the highest k values reported using TiO_2 nanostructured films [12].

Three samples of the former series (sintered at $T_s = 450, 490$ and 550°C) were chemically etched (CE) by immersion during 25 s in diluted hydrochloric acid. Fig. 9 shows the diffraction patterns of these films. One can see that the three films are only constituted of CdTiO_3 . The [MB] normalized as a function of T_s for the samples without CE and with CE and an exposure time of 5 h, is plotted in Fig. 10. In all cases, the PA is lower in the samples with CE than without CE. This last result indicates to us that it is important to have both oxides in order to reach the best photocatalytic activity. A mechanism of coupling between the crystalline grains of CdO and CdTiO_3 can be responsible for the PA enhancement. According to X-ray measurements, not a lot of CdO is present in the film after etching, therefore, it is plausible to assume that CdTiO_3 grains predominates in the film and, for this reason, the photocatalytic activity decreases. This result confirms that coupling of energy band gaps of CdO and CdTiO_3 enhanced the photocatalytic effect of the films.

A possible simplified process of coupling between CdO and CdTiO_3 for charge separation is proposed, if doping effect is not considered to occur in both oxides during the growth [13–16]. Relatively recent several values have been published on electron affinity (χ) of CdO: 4.51 eV [17], 5.0 eV [18] and 5.94 eV [19]. The average $\chi_{\text{CdO}} = 5.2$ will be taken by us as an acceptable value. For CdTiO_3 , as far as we know, no value of χ has been reported. However, according to Campet et al. [20] titanates have similar values and if published values in the literature for these oxides are taken into account: $\chi_{\text{BaTiO}_3} = 3.9$ eV [21,22]; $\chi_{\text{SrTiO}_3} = 3.4$ eV [20], 3.2 eV

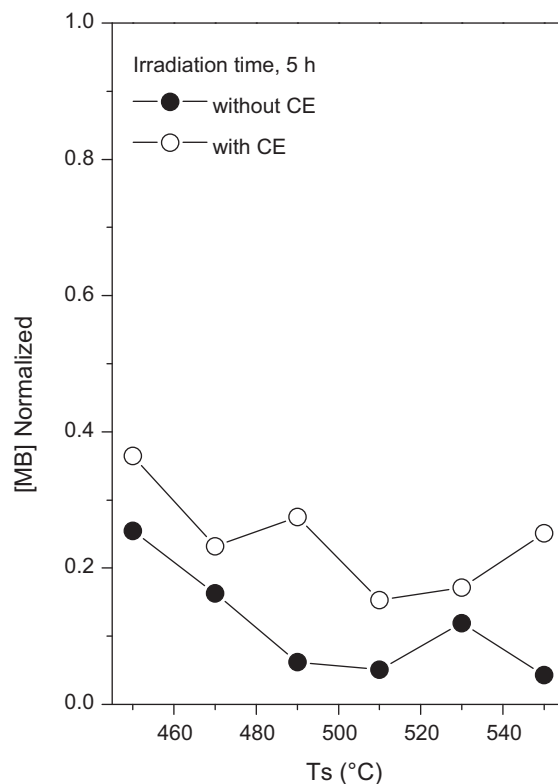


Fig. 10. [MB] normalized as a function of T_s for the samples without chemical etching (CE) and with CE.

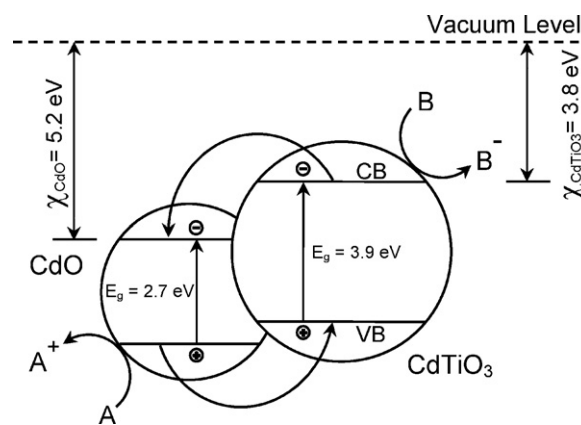


Fig. 11. Diagram illustrating the principle of charge separation in the CdO– CdTiO_3 coupled semiconductor system.

[21] and 4.1 eV [18]; $\chi_{\text{ZnTiO}_3} = 4.0$ eV [23]; $\chi_{\text{PbTiO}_3} = 3.5$ eV [21,24]. These results suggest to take $\chi_{\text{CdTiO}_3} = 3.8$ eV as an acceptable average from these oxides for χ of CdTiO_3 . With this value a probable process for separation of charges is shown in Fig. 11.

4. Conclusions

The films are polycrystalline and they are constituted of two oxides, CdO and CdTiO_3 . The quantity of each of them depends on the sintering temperature. The films are opaque indicating that the surface of all the films is rough and consequently the transmission is relatively low. The films sintered at $T_s = 490^\circ\text{C}$ and 550°C show the best photocatalytic activities and their grain size values are very similar. When the CdO is removed from each of the films (by chemical etching) the photocatalytic activity decreases with respect to

films without chemical etching. A mechanism of coupling between the crystalline grains of CdO and CdTiO₃ can be the reason for such a decrease.

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References

- [1] D. Bahnemann, D. Bockelmann, R. Golish, M. Hilgendorff, D. Weichgrebe, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 301.
- [2] I. Poulos, D. Makri, X. Prohaska, Photocatalytic treatment of olive milling waste water: oxidation of protocatechuic acid, *Global Nest: Int. J.* 1 (1999) 55–62.
- [3] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO₂, *Sol. Energy Mater. Sol. Cells* 77 (2003) 65–82.
- [4] C. Karunakaran, S. Senthilvelan, Semiconductor catalysis of solar photooxidation, *Curr. Sci.* 88 (2005) 962–967.
- [5] H.B. Lu, L. Liao, H. Li, Y. Tian, D.F. Wang, J.C. Li, Q. Fu, B.P. Zhu, Y. Wu, Fabrication of CdO nanotubes via simple thermal evaporation, *Mater. Lett.* 62 (2008) 3928–3930.
- [6] A.L. Lisebigler, G. Lu, J.T. Yates Jr., Photocatalysis on TiO₂ surfaces: principles, mechanisms and selected rules, *Chem. Rev.* 95 (1995) 735–758.
- [7] S. Hotchandani, P.V. Kamat, Charge–transfer processes in coupled semiconductor systems–photochemistry and photoelectrochemistry of the colloidal CdS–ZnO system, *J. Phys. Chem.* 96 (1992) 6834–6839.
- [8] S.A. Mayén Hernández, G. Torres Delgado, R. Castanedo Pérez, J.G. Mendoza Alvarez, O. Zelaya Ángel, Effect of the sintering temperature on the photocatalytic activity of CdO + CdTiO₄ thin films, *J. Adv. Oxid. Technol.* 10 (2007) 85–89.
- [9] S.A. Mayén Hernández, G. Torres Delgado, R. Castanedo Pérez, A. Cruz Orea, J.G. Mendoza Alvarez, O. Zelaya Angel, CdO + CdTiO₄ thin films prepared by sol–gel, *Sol. Energy Mater. Sol. Cells* 90 (2006) 2280–2288.
- [10] M.A. Yakubovskii, V.I. Zametin, L.M. Rabkin, Absorption-edge of CdTiO₃, *Sov. Phys. J.* 21 (1978) 133–135.
- [11] D.M. Carballeda Galicia, R. Castanedo Pérez, O. Jiménez Sandoval, S. Jiménez Sandoval, G. Torres Delgado, C.I. Zúñiga Romero, High transmittance CdO thin films obtained by the sol–gel method, *Thin Solid Films* 371 (2000) 105–108.
- [12] T.-D. Nguyen-Phan, V.H. Pham, T.V. Cuong, S.H. Hahn, E.J. Kim, J.S. Chung, S.H. Hur, E.W. Shin, Fabrication of TiO₂ nanostructured films by spray deposition with high photocatalytic activity of methylene blue, *Mater. Lett.* 64 (2010) 1387–1390.
- [13] H.Y. Yang, S.F. Yu, S.P. Lau, X. Zhang, D.D. Sun, G. Jun, Direct growth of ZnO nanocrystals on the surface of porous TiO₂ nanotube arrays for highly efficient and recyclable, *Small* 5 (2009) 2260–2264.
- [14] L. Xu, H. Shen, X. Li, R. Zhu, Enhanced ultraviolet emission from ZnO thin films covered by TiO₂ nanoparticles, *Chin. Opt. Lett.* 7 (2009) 953–955.
- [15] K. Vinodgopal, P.V. Kamat, Enhanced rates of photocatalytic degradation of an Azo dye using SnO₂/TiO₂ coupled semiconductor thin films, *Environ. Sci. Technol.* 29 (1995) 841–845.
- [16] L. Jin, B. Xin, F. Yuan, L. Xue, B. Wang, H. Fu, Effects of surface oxygen vacancies on photophysical and photochemical processes of Zn-doped TiO₂ nanoparticles and their relationship, *J. Phys. Chem. B* 110 (2006) 17860–17865.
- [17] R. Ferro, J.A. Rodríguez, Influence of F-doping on the transmittance and electron affinity of CdO thin films suitable for solar cells technology, *Sol. Energy Mater. Sol. Cells* 64 (2000) 363–370.
- [18] J. Robertson, S.J. Clark, Limits doping in oxides, *Phys. Rev. B* 83 (7) (2011) 075205.
- [19] D.T. Speaks, M.A. Mayer, K.M. Yu, S.S. Mao, E.E. Haller, W. Walukiewicz, Fermi stabilization energy in cadmium oxide, *J. Appl. Phys.* 107 (2010) 113706.
- [20] G. Campet, J.P. Manaud, C. Puprichitkun, Z.W. Sun, P. Salvador, Protection anodes against photocorrosion by surface deposition of oxide films: criteria for choosing the protective coating, *Active Passive Electr. Comp.* 13 (1989) 175–189.
- [21] P.W. Peacock, J. Robertson, Band offsets and Schottky barrier heights of high dielectric constant oxides, *J. Appl. Phys.* 92 (2002) 4712–4721.
- [22] G.Y. Yang, E.C. Dickey, C.A. Randall, D.E. Barber, P. Pinceloup, M.A. Henderson, R.A. Hill, J.J. Beeson, D.J. Skamser, Oxygen nonstoichiometry and dielectric evolution of BaTiO₃. Part I. Improvement of insulation resistance with reoxidation, *J. Appl. Phys.* 96 (2004) 7492–7499.
- [23] Y. Xu, M.A.A. Schoonen, The absolute energy positions of conduction and valence bands of selected semiconducting minerals, *Am. Mineral.* 85 (2000) 543–556.
- [24] P. Erhart, R.A. Eichel, P. Träskelin, K. Albe, Association of oxygen vacancies with impurity metal ions in lead titanate, *Phys. Rev. B* 76 (2008) 174116.